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jc915 U.S. PTO 09/695194 10/24/00

UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No.	M8540/248465
First Named Inventor or Application Identifier	Gary Anthony Jubb
Title	Saline Soluble Inorganic Fibres
Express Mail Label No.	EL568948202US

APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents

ADDRESS TO: Assistant Director for Patents
Box Patent Application
Washington, D.C 20231

1. ☒ Fee Transmittal Form (*e.g. PTO/SB/17*)
   (Submit an original, and a duplicate for fee processing)
2. ☐ Applicant claims small entity status. See 37 CFR 1.27
3. ☒ Specification Total Pages 48
   (*preferred arrangement as set forth below*)
   - Descriptive title of the Invention
   - Cross References to Related Applications
   - Statement Regarding Fed sponsored R & D
   - Reference to sequence listing, a table, or a computer program listing appendix
   - Background of the Invention
   - Brief Summary of the Invention
   - Brief Description of the Drawings (*if filed*)
   - Detailed Description
   - Claim(s)
   - Abstract of the Disclosure
4. ☒ Drawing(s) (*35 U.S.C. 113*) [*Total Sheets*] 05
5. ☒ Oath or Declaration [*Total Pages*] 02
   a. ☐ Newly executed (original or copy)
   b. ☒ Copy from a prior application (37 CFR 1.63(d)) (*for continuation/divisional with box 17 completed)*
      i. ☐ DELETION OF INVENTOR(S)
      Signed statement attached deleting inventor(s) named in the prior application, See 37 C.F.R. 1.63(d)(2) and 1.33(b).
6. ☐ Application Data Sheet. See 37 CFR 1.76
7. ☐ CD-ROM or CD-R in duplicate, large table or Computer Program (*Appendix*)
8. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
   a. ☐ Computer Readable Copy (CRF)
   b. ☐ Specification Sequence Listing on:
      i. ☐ CD-ROM or CD-R (2 copies); or
      ii. ☐ Paper
   c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

9. ☒ Assignment Papers (cover sheet & document(s))
10. ☐ 37 CFR 3.73(b) Statement ☒ Power of Attorney (*when there is an assignee*)
11. ☐ English Translation Document (*if applicable*)
12. ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
13. ☒ Preliminary Amendment
14. ☒ Return Receipt Postcard (MPEP 503) (*Should be specifically itemized)*
15. ☐ Certified Copy of Priority Document(s) (*If foreign priority is claimed*)
16. ☒ Other:
    Appointment of Associate Attorney
    Transmittal of Formal Drawings
    Substitute Combined Declaration and Power of Attorney

17. If a CONTINUING APPLICATION, *check appropriate box and supply the requisite information below and in a preliminary amendment, or in an Application Data Sheet under 37 CFR 1.76:*

☐ Continuation ☒ Divisional ☐ Continuation-in-part (CIP) of prior application No.: 09/262,378

Prior application information: Examiner: K. Group Group/Art Unit: 1755

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

18. CORRESPONDENCE ADDRESS

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Name	John S. Pratt				
	KILPATRICK STOCKTON LLP				
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Country	U.S.A.	*Telephone*	404.815.6500	*Fax*	404.815.6555

Name (Print/Type)	Bruce D. Gray	Reg. No.	35,799
Signature		Date	10/24/00

23370
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FEE TRANSMITTAL for FY 2000

Patent fees are subject to annual revision

Small Entity payments must be supported by a small entity statement, otherwise, large entity fees must be paid.

See 37 C.F.R. §§ 1.27 and 1.28

TOTAL AMOUNT OF PAYMENT ($)710.00

Complete if Known	
Application Number	Divisional of 09/262,378
Filing Date	October 24, 2000
First Named Inventor	Gary Anthony Jubb
Group / Art Unit	1755
Examiner Name	Group, K.
Attorney Docket Number	M8540/248465

JC925 U.S. PTO 09/695194 10/24/00

METHOD OF PAYMENT (check one)

1. ☒ The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

Deposit Account Number: 11-0855

Deposit Account Name: KILPATRICK STOCKTON LLP

☒ Charge any Additional Fee Required Under 37 CFR 1 16 and 1 17

☐ **Applicant claims small entity status. See 37 CFR 1.27**

2. ☒ Payment Enclosed:

☒ Check ☐ Credit Card ☐ Money Order ☐ Other

FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
101	710	201	355	Utility filing fee	710.00
106	310	206	155	Design filing fee	
107	480	207	240	Plant filing fee	
108	690	208	345	Reissue filing fee	
114	150	214	75	Provisional filing fee	

SUBTOTAL (1) ($)710.00

2. EXTRA CLAIM FEES

			Extra Claims		Fee from below		Fee Paid
Total Claims	09	-20**=	00	x		=	.00
Independent Claims	01	-3**=	00	x		=	.00
Multiple Dependent Claims							

** or number previously paid, if greater, For Reissues, see below

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description
103	18	203	9	Claims in excess of 20
102	78	202	39	Independent claims in excess of 3
104	260	204	130	Multiple dependent claim
109	78	209	39	**Reissue independent claims over original patent
110	18	210	9	**Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) ($)0

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Large Entity Fee ($)	Small Entity Fee Code	Small Entity Fee ($)	Fee Description	Fee Paid
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet	
139	130	139	130	Non-English Specification	
147	2,520	147	2,520	For filing a request for *ex parte* reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	380	216	190	Extension for reply within second month	
117	870	217	435	Extension for reply within third month	
118	1,360	218	680	Extension for reply within fourth month	
128	1,850	228	925	Extension for reply within fifth month	
119	300	219	150	Notice of appeal	
120	300	220	150	Filing a brief in support of an appeal	
121	260	221	130	Request for oral hearing	
138	1,510	138	1,510	Petition to institute a public use hearing	
140	110	240	55	Petition to revive - unavoidable	
141	1,210	241	605	Petition to revive - unintentional	
142	1,210	242	605	Utility issue fee (or reissue)	
143	430	243	215	Design issue fee	
144	580	244	290	Plant issue fee	
122	130	120	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	240	126	240	Submission of Information Disclosure Statement	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	690	246	345	Filing a submission after final rejection (37 CFR 1.129(a))	
149	690	249	345	For each additional invention to be examined (37 CFR 1.129(b))	
179	690	279	345	Request for Continued Examination (RCE)	

Other fee (specify)__________

*Reduced by Basic Filing Fee Paid **SUBTOTAL (3)** ($)

SUBMITTED BY		Complete (if applicable)			
Typed or printed Name	Bruce D. Gray Kilpatrick Stockton LLP	Reg. No (Attorney/Agent)	35,799		
		Customer No. 23370	Telephone	(404) 815-6218	
Signature	[signature]		Date	10/24/00	

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1047471

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Gary Anthony Jubb and Jean-Louis Martin

Serial No.: Divisional of 09/262,378

Filing Date: October 24, 2000

For: SALINE SOLUBLE INORGANIC FIBRES

Box Patent Application
Director of Patents and Trademarks
Washington, D.C. 20231

Date: October 24, 2000

PRELIMINARY AMENDMENT

Sir:

Preliminary to any examination on the merits, Applicants respectfully submit the following amendments and remarks:

In the Specification

Kindly add the following paragraph immediately preceding line 1:

--This application is a divisional of U.S. Serial No. 09/262,378 filed March 4, 1999, now allowed, which is a continuation of U.S. Serial No. 08/899,005 filed July 23, 1997, now U.S. Patent No. 5,994,247 issued on November 30, 1999, which is a continuation of U.S. Serial No. 08/535,587 filed September 28, 1995, now abandoned, which is a continuation of U.S. Serial No. 08/039,086, filed April 9, 1993, now abandoned, which claims priority to International Application No. PCT/GB93/00085, filed January 15, 1993, which claims priority to GB 92 00993.5, filed January 17, 1992 and GB 92 24612.3, filed November 24, 1992--.

In the Claims

Please cancel claims 1-13 without prejudice or disclaimer to the subject matter thereof.

Please add the following new claims.

--14. A method of insulating an article against temperatures which may on occasion exceed 900°C comprising:

disposing on, in, near or around the article thermal insulation which is a refractory insulating material having a maximum service temperature greater than 900°C and comprising vitreous fibers having a composition comprising SiO_2, CaO, MgO, and optionally Al_2O_3, wherein:

(a) SiO_2 is present in an amount (1) greater than 58% by weight SiO_2, if the amount of MgO in the composition is in the range 0 through 10 percent by weight; or (2) greater than the sum of (58 + 0.5(weight percent of MgO - 10)) percent by weight SiO_2, if the amount of MgO in the composition is greater than 10 percent by weight;

(b) an amount up to 42 percent by weight CaO;

(c) an amount up to 31.33 percent by weight MgO., and

(d) 0 to less than 3.97 percent by weight Al_2O_3;

wherein the refractory insulation material has a maximum service temperature greater than 900°C; the refractory insulation material has a shrinkage of less than 3.5 percent when exposed to a temperature of 1000°C for 24 hours, and has a shrinkage of less than 3.5 percent when exposed to a temperature of 800°C for 24 hours; and

wherein the refractory insulation material is essentially free of alkali metal oxide and boron oxide fluxing components.--

--15. The method of claim 14, wherein the amount of SiO_2 is less than 70 percent by weight. --

--16. The method of claim 14, wherein the vitreous fibers crystallize as wollastonite, pseudowollastonite, or a mixture thereof after exposure to a temperature of 1000°C, and wherein said wollastonite, pseudowollastonite, or mixture thereof comprises:

(a) 60 through 67 percent by weight SiO_2;

(b) 26 through 35 percent by weight CaO;

(c) 4 through 6 percent by weight MgO; and

(d) 0 through 3.5 percent by weight Al_2O_3. --

--17. The method of claim 14, wherein the vitreous fibers comprise:

(a) a maximum of 71.24 percent by weight SiO_2;

(b) 4.46 through 34.49 percent by weight CaO;

(c) 1.71 through 22.31 percent by weight MgO; and

(d) 0 through 2.57 percent by weight Al_2O_3. --

--18. The method of claim 17, wherein the vitreous fibers further comprise:

(e) 0 through 0.65 percent by weight Na_2O;

(f) 0 through 0.13 percent by weight K_2O;

(g) 0.08 through 0.4 percent by weight Fe_2O_3; and

(h) 0 through 1.23 percent by weight ZrO_2. --

--19. The method of claim 14, further comprising forming said vitreous fibers into a bulk, blanket, block, or vacuum-formed form.--

--20. The method of claim 14, wherein said insulated article is occasionally exposed to a temperature above around 1000°C.--

--21. The method of claim 19 wherein said vitreous fibers are formed into a needled blanket.--

--22. The method of claim 14, wherein the vitreous fibers crystallize as diopside after exposure to a temperature of 1000°C, and wherein said diopside comprises:

(a) 59 through 64 percent by weight SiO_2;

(b) 19 through 23 percent by weight CaO;

(c) 14 through 17 percent by weight MgO; and

(d) 0 through 3.5 percent by weight Al_2O_3.--

REMARKS

New claims 14-22 are fully supported by the specification as originally filed, and correspond to claims 23-28, 30, and 31 in parent application Serial No. 09/262,378. No new matter has been added.

Applicants respectfully submit that the claims are novel and nonobvious over Olds et al. (U.S. Patent No. 5,332,699), Olds et al. (WO 87/05007), or Karppinen et al., and that the rejections made by the Examiner over these references in the parent application should not be repeated.

The claims recite a process for insulating an article against temperatures that may exceed 900 °C. None of the above references teach insulating against such a high temperature, which is

quite different from insulating against another, lower temperature. As a result, the references do not anticipate the claimed invention. Moreover, there is no teaching or suggestion to use the materials described in the above references to insulate against such high temperatures. In particular, there is no teaching or suggestion that the materials described in the references would be able to withstand temperatures that exceed 900 °C without shrinking. As the Examiner is no doubt aware, even if a fiber can withstand high temperatures, if it shrinks substantially when exposed to those temperatures, then its value as insulation is very low, since the shrinkage will cause gaps in the insulation.

Applicants respectfully submit that the claims are in condition for allowance, and an early notification to that effect is earnestly solicited.

Please charge any additional fees or credit any overpayment to Deposit Order Account No. 11-0855.

Respectfully submitted,

Bruce D. Gray
Reg. No. 35,799

Attorney for Assignee

OF COUNSEL:
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Suite 2800
1100 Peachtree Street
Atlanta, Georgia, 30309-4530
404-815-6218
Attorney Docket No.: M8540/248465

SALINE SOLUBLE INORGANIC FIBRES

This invention relates to saline soluble. non-metallic, amorphous, inorganic oxide, refractory fibrous materials.

Inorganic fibrous materials are well known and widely used for many purposes (e.g. as thermal or acoustic insulation in bulk, mat, or blanket form, as vacuum-formed shapes, as vacuum formed boards and papers, and as ropes, yarns or textiles; as a reinforcing fibre for building materials; as a constituent of brake blocks for vehicles). In most of these applications the properties for which inorganic fibrous materials are used require resistance to heat, and often resistance to aggressive chemical environments.

Inorganic fibrous materials can be either glassy or crystalline. Asbestos is an inorganic fibrous material one form of which has been strongly implicated in respiratory disease.

It is still not clear what the causative mechanism is that relates some asbestos with disease but some researchers believe that the mechanism is mechanical and size related. Asbestos of a critical size can pierce cells in the body and so, through long and repeated cell injury, have a bad effect on health.

Whether this mechanism is true or not regulatory agencies have indicated a desire to categorise any inorganic fibre product that has a respiratory fraction as 'hazardous', regardless of whether there is any evidence to support such categorisation. Unfortunately for many of the applications for which inorganic fibres are used, there are no realistic substitutes.

Accordingly there is a demand for inorganic fibres that will pose as little risk as possible (if any) and for which there are objective grounds to believe them safe.

A line of study has proposed that if inorganic fibres were made that were sufficiently soluble in physiological fluids that their residence time in the human body was short; then damage would not occur or at least be minimised. As the risk of asbestos-linked disease appears to depend very much on the length of exposure this idea appears reasonable. Asbestos is extremely insoluble.

As intercellular fluid is saline in nature the importance of fibre solubility in saline solution has long been recognised. If fibres are soluble in physiological saline solution then, provided the dissolved components are not toxic, the fibres should be safer than fibres which are not so soluble. The shorter the time a fibre is resident in the body the less damage it can do. H. Förster in 'The behaviour of mineral fibres in physiological solutions' (*Proceedings of 1982 WHO IARC Conference*, Copenhagen, Volume 2, pages 27-55(1988)) discussed the behaviour of commercially produced mineral fibres in physiological saline solutions. Fibres of widely varying solubility were discussed.

International Patent Application No. WO87/05007 disclosed that fibres comprising magnesia, silica, calcia and less than 10 wt% alumina are soluble in saline solution. The solubilities of the fibres disclosed were in terms of parts per million of silicon (extracted from the silica-containing material of the fibre) present in a saline solution after 5 hours of exposure. The highest value revealed in the examples had a silicon level of 67 ppm. In contrast, and adjusted to the same regime of measurement, the highest level disclosed in the Förster paper was equivalent to approximately 1 ppm. Conversely if the highest value revealed in the International Patent Application was converted to the same measurement

regime as the Förster paper it would have an extraction rate of 901,500 mg Si/kg fibre - i.e. some 69 times higher than any of the fibres Förster tested, and the fibres that had the highest extraction rate in the Förster test were glass fibres which had high alkali contents and so would have a low melting point. This is convincingly better performance even taking into account factors such as differences in test solutions and duration of experiment.

International Patent Application No. WO89/12032 disclosed additional fibres soluble in saline solution and discusses some of the constituents that may be present in such fibres.

European Patent Application No. 0399320 disclosed glass fibres having a high physiological solubility.

Further patent specifications disclosing selection of fibres for their saline solubility are European 0412878 and 0459897, French 2662687 and 2662688, PCT WO86/04807 and WO90/02713.

The refractoriness of the fibres disclosed in these various prior art documents varies considerable. The maximum service temperature of any of these disclosed fibres (when used as refractory insulation) is up to 815°C (1500°F).

Service temperature for refractory insulation is definable in many ways but to be consistent with the above mentioned International Patent Applications this application shall mean by service temperature that temperature at which the fibre shows acceptable shrinkage (maximum of 5% linear shrinkage after exposure to temperature for 24 hours) and at which the fibre has not appreciably suffered through excessive sintering or softening.

There is a demand for physiologically soluble fibres having a service temperature of greater than 815°C,

particularly for such fibres having a service temperature above 900°C.

Testing for physiological solubility and safety can be done by inhalation studies on, e.g. rats. However such studies are extremely time consuming and costly. A study can take of the order of 2½ years from start and can easily cost £1 million per study. A cheaper alternative is to test for solubility in physiological or like fluids *in vitro*.

Testing of an inorganic fibre for solubility in physiological solutions is not so time consuming, but there is currently no way of predicting which systems will produce such soluble fibres. Therefore anyone seeking to find such soluble fibres has to work on a trial and error basis assisted by what is commonly known as 'chemical intuition' but is equally commonly known as 'a hunch'. Such trial and error testing is laborious and time consuming. Further, once a fibre is found that is soluble there is no guarantee that it will be usable at useful service temperatures.

Accordingly there is a demand for a method of predicting whether a fibre will have a reasonable solubility in physiological solutions, and further there is a demand that such a test should preferably give an indication as to expected service temperature.

Shrinkage of inorganic refractory fibres occurs through two mechanisms; the first is viscous flow of the fibre material. Most inorganic refractory fibres are glasses and so may be defined as liquids having an exceedingly high viscosity (but still liable to flow). By their nature fibres are elongate and so have a high surface area per unit volume. As the reduction of surface area is a means of reducing the surface energy of a material, when the glass becomes fluid enough it will flow so as to reduce surface area. This flow results in a coarsening and shortening of the fibres and so to

shrinkage, and in the extreme results in disruption of the fibres into separate particles.

The second mechanism leading to shrinkage is that at elevated temperatures glasses may crystallise to form one or more crystal phases. Usually these crystal phases have a smaller molar volume than the glasses from which they crystallise and so shrinkage results. Some fibres are known for which the molar volume of the crystalline form exceeds that of the glass (for example Al_2O_3/SiO_2 glassy fibres may crystallise to form mullite crystals). In these cases the expansion due to crystallisation may oppose the shrinkage caused by viscous flow.

If shrinkage through viscous flow occurs at a much lower temperature than crystallisation then the crystallisation may not be able to compensate for such shrinkage.

There is a demand for a fibre in which both viscous flow and crystallisation occur at as high and as similar a temperature as possible, and preferably in which the expansion due to crystallisation closely matches the shrinkage due to viscous flow so that the net effect is as close to zero shrinkage as possible.

When used as refractory insulation inorganic refractory fibres are used in several forms. The fibres may be supplied as a bulk material, but in this form the fibres are difficult to handle for many applications. Alternatively the fibre may be supplied as a blanket. Blanket fibre is generally made by a process of sucking fibre from air onto a conveyor to form a blanket. Because the fibres tend to be aligned parallel to the conveyor surface they can separate easily. Accordingly the blanket fibres are secured together by adding a binder to lock the fibres together, or by needling the blanket, or both. In needling needles are passed through the thickness of the blanket to push and draw fibres to lie transverse to the

blanket and so tie the fibres together. Because binders are usually resins, such as phenolic resins, they burn off on first firing. There is a desire to reduce the amount of such binders used both because of possible health implications in handling, and because the combustion products may affect the strength of the fibres. Thus needled blanket is usually preferred.

The fibres may also be supplied as blocks, generally made from assembled layers of inorganic fibre blanket.

For some fibres needling is not possible. Crystalline fibres are generally too brittle to stand the stresses involved. For the fibres known in the industry as glass fibres (which are generally used for low temperature applications) the amount of 'shot' (unfiberised glass particles) present is generally too high to allow needling as the shot damages the needles. There is no needled blanket on the market that has a maximum service temperature in the range 900°C-1200°C. There are needled blankets having a higher maximum service temperature but these use expensive fibres in comparison with other fibres usable (with the aid of binders) as blanket in the temperature range 900°C-1200°C.

Accordingly there is a demand for needled fibre blanket formed from inexpensive materials, being soluble in saline solutions, and having a maximum service temperature in the range 900°C-1200°C.

As stated previously refractory oxide fibres are made by several methods all of which involve the formation of a melt of oxides and the subsequent fiberisation of the melt by e.g. spinning or blowing.

The melt of oxide material is often formed by electrical discharge melting of the constituent raw materials. The applicants, in manufacture of a $CaO/MgO/SiO_2$ refractory oxide

fibre encountered problems due to the necessity of handling CaO. These problems were discovered to be due to the moisture content of CaO as commercially available. One of the problems of use of CaO is the outgasing that results upon melting and this led at the least to a porous melt pool which caused fluctuations in the melt current; in the extreme the outgasing was explosive. Additionally use of CaO appeared to cause accelerated attack on the melt electrodes. Also CaO is a difficult and corrosive material to handle.

Accordingly there is a need for a process that minimises the use of CaO.

Accordingly the present invention provides the following features both independently and in combination:-

A. Use of a vitreous inorganic fibre in the knowledge that it has a composition meeting the criteria either:- that the calculated sum of the free energies of hydration of the compounds that would or could be present at equilibrium (on the basis of knowledge, informed belief or reasonable assumption) is more negative than -10 kcal/100grams (-418.4kJ/kg) of composition; or that the percentage of non-bridging oxygens is more than 30%. Such compositions tend to be saline soluble.

B. Use of such a vitreous inorganic fibre in the knowledge that it has a composition meeting the criterion that the ratio of glass modifiers to network formers is less than a critical value (for SiO_2 based compositions the critical value is 1). Such compositions tend to be glass formers.

C. The invention also encompasses fibres selected by adopting such criteria as a test for solubility and glass formation.

D. Use as saline soluble fibres having a shrinkage of less

than 3.5% when exposed to 1000°C for 24 hours and/or 800°C for 24 hours, of vitreous fibres having a composition comprising (in weight %):-

SiO_2	>58%	- (for MgO =< 10%) and
SiO_2	>58% + 0.5(%MgO -10)	- (for MgO >= 10%)

(SiO_2 preferably being below 70%)

CaO	0% - 42%
MgO	0% - 31.33%
Al_2O_3	0% - <3.97%

and being essentially free of fluxing components such as alkali metals and boron oxide.

E. In one such usage the first crystalline material resulting on crystallisation has the crystal structure of diopside and has the composition consisting essentially of:-

Component	Composition A Weight percent
SiO_2	59-64
Al_2O_3	0-3.5
CaO	19-23
MgO	14-17

F. In a second such usage the first crystalline material resulting on crystallisation has the crystal structure of wollastonite/pseudowollastonite and has the composition consisting essentially of:-

Component	Composition B Weight percent
SiO_2	60-67
Al_2O_3	0-3.5
CaO	26-35
MgO	4-6

G. The fibres used in such manner may further be used as needled blankets.

H. Preferably the fibres of the general composition and compositions A and B mentioned above have a SiO_2 content (expressed as a weight percentage of the constituents SiO_2, CaO and MgO) of greater than 60%.

I. The present invention further provides a method for the manufacture of refractory oxide fibres containing calcium and silicon by the formation of an oxide melt containing calcium and silicon characterised in that all or part of the calcium and all or part of silicon is provided by a calcium silicate.

The invention is illustrated by way of example in the following description and with reference to the drawings in which:-

Fig.1 is a three-axis phase diagram indicating the crystalline phases in the system SiO_2/CaO/MgO (*Phase Diagrams for Ceramists*, The American Ceramic Society, 1964) a key to this diagram is at the end of the specification;

Fig.2 is a three-axis composition plot of the projection onto the SiO_2/CaO/MgO phase field of compositions comprising SiO_2, CaO, MgO and Al_2O_3;

Fig.3 is a temperature/time plot of the firing regime used in a series of cyclic exposure tests of experimental

compositions;

Fig.4 is a plot of log (total solubility) v calculated free energy of hydration for a series of fibres.

Fig.5 is a plot of log (total solubility) v % non-bonding oxygens for a series of fibres (see below).

A series of fibres were made of the compositions shown in Table 1. These fibres were melt spun by using a vertical spinning system of the type known for making inorganic fibres. Also shown in Table 1 are the compositions of some comparative commercially available inorganic oxide fibres and glass fibres.

TABLE 1

	Al_2O_3	SiO_2	CaO	MgO	ZrO_2
SW-A	3.3	59.3	20.5	15.5	-
SW-A1	1.1	63.7	20.5	15.2	-
SW-A2	0.8	60.8	21.4	15.4	-
SW-B1	2.3	65.3	26.8	5.7	-
SW-B2	1.3	66.9	27.5	5.2	-
SW-B3	1.0	60.0	34.0	4.4	-

COMPARATIVE EXAMPLES

	Al_2O_3	SiO_2	CaO	MgO	ZrO_2	MST
CRBT	46.5	53	0.04	0.01	-	1260°C
CWBT	40.6	49.5	5.50	4.00	-	870°C
CHBT	49.7	35.1	0.04	0.01	14.7	1425°C
Glass Fibre	15.2/ 15.5	53.7/ 57.5	21.1/ 21.8	1.3/ 1.6	-	+ 5.9-6.2% B_2O_3 0.11-0.12% TiO_2 0.46% Na_2O 0.32-0.33% K_2O
Needled Glass Fibre	3.7	60.5/ 60.0	8.1 7.9	4.0	- -	+ 2.85-2.95% B_2O_3 13.5% Na_2O 1.0% K_2O

[MST = Maximum Service Temperature (oxidising atmosphere)]

The fibres SW-A, SW-A1, SW-A2, SW-B1, SW-B2 and SW-B3 were tested for solubility by the following method.

The fibre was first chopped in the following manner. 2.5 g of fibre (deshotted by hand) was liquidised with 250 cm^3 of distilled water in a domestic Moulinex (Trade Mark) food blender for 20 seconds. The suspension was then transferred to a 500 cm^3 plastic beaker and allowed to settle after which as much liquid as possible was decanted and the remaining liquid removed by drying in an oven at 110°C.

The solubility test apparatus comprised a shaking incubator water bath, and the test solution had the following composition:-

Compound	Name	Grams
NaCl	Sodium chloride	6.780
NH_4Cl	Ammonium chloride	0.540
$NaHCO_3$	Sodium bicarbonate	2.270
$Na_2HPO_4.H_2O$	Disodium hydrogen phosphate	0.170
$Na_3C_6H_5O_{7p}.2H_2O$	Sodium citrate dihydrate	0.060
$H_2NCH_2CO_2H$	Glycine	0.450
H_2SO_4 s.g. 1.84	Sulphuric acid	0.050

The above materials were diluted to 1 litre with distilled water to form a physiological-like saline solution.

0.500 grams ± 0.0003 grams of chopped fibre was weighed into a plastic centrifuge tube and 25 cm^3 of the above saline solution added. The fibre and saline solution was shaken well and inserted into the shaking incubator water bath maintained at body temperature (37°C ± 1°C). The shaker speed was set at 20 cycles/minute.

After the desired period (usually 5 hours or 24 hours)

the centrifuge tube was removed and centrifuged at ≈ 4500 revs/minute for approximately 5 minutes. Supernatant liquid was then drawn off using a syringe and hypodermic needle. The needle was then removed from the syringe, air expelled from the syringe, and the liquid passed through a filter (0.45 micron cellulose nitrate membrane filter paper [WCN type from Whatman Labsales Limited]) into a clean plastic bottle. The liquid was then analysed by atomic absorption using a Thermo Jarrell Ash Smith - Hiefje II machine.

The operating conditions were:-

ELEMENT	WAVELENGTH(nm)	BAND WIDTH	CURRENT(MA)	FLAME (Nitrous Oxide + Acetylene)
Al	309.3	1.0	8	Fuel Rich
SiO_2	251.6	0.3	12	" "
CaO	422.7	1.0	7	Fuel Lean
MgO	285.2	1.0	3	" "

The procedure and standards adopted for determining the above elements were as set out below.

SiO_2 can be determined without dilution up to 250 ppm concentration (1 ppm ≡ 1mg/Litre). Above this concentration an appropriate dilution was made volumetrically. A 0.1% KCl solution (0.1g in 100 cm^3) was added to the final dilution to prevent ionic interference. <u>NB</u> If glass apparatus is used, prompt analysis is necessary.

From a stock solution of 1000 ppm pure ignited silica (99.999%) (fused with Na_2CO_3 at 1200°C for 20 minutes in a platinum crucible (0.2500g SiO_2/2g Na_2CO_3) and dissolved in dilute hydrochloric acid (4 molar) made up to $250cm^3$ with distilled water in a plastic volumetric flask) the following

standards were produced:-

STANDARD (PPM SiO_2)	STOCK SOLUTION (cm^3)
10.0	1.0
20.0	2.0
30.0	3.0
50.0	5.0
100.0	10.0
250.0	25.0

Add 0.1% KCl to each standard before making to $100cm^3$.

Aluminium may be measured directly from the sample without dilution. Standards of 1.0, 5.0 and 10.0 ppm Al may be used. For calibration readings are multiplied by 1.8895 to convert from Al to Al_2O_3.

A standard Al atomic absorption solution (e.g. BDH 1000 ppm Al) was bought and diluted using an accurate pipette to the desired concentration. 0.1% KCl was added to prevent ionic interference.

Calcium may require dilutions on the sample before determination can be carried out (i.e. x 10 and x 20 dilutions). Dilutions must contain 0.1% KCl.

A standard Ca atomic absorption solution (e.g. BDH 1000 ppm Ca) was diluted with distilled water and an accurate pipette to give standards of 0.5, 4.0 and 10.0 ppm. 0.1% KCl is added to prevent ionic interference. To convert readings obtained from Ca to CaO a factor of 1.4 was used.

Magnesium may require dilutions on the sample before determinations can be made (i.e. x 10 and x 20). Add 0.1% KCl to each dilution. To convert Mg to MgO multiply by 1.658.

A standard Mg atomic absorption solution (e.g. BDH 1000 ppm Mg) was diluted with distilled water and an accurate

pipette to give standards of 0.5, 1.0 and 10.0 ppm Mg. 0.1% KCl was added to prevent ionic interference.

All stock solutions were stored in plastic bottles.

The results of the tests are indicated in Table 2.

TABLE 2

BODY FLUIDS SOLUBILITY
(ppm)

	SiO_2		CaO		MgO	
	5h	24h	5h	24h	5h	24h
SW-A	98	120	63	56	33	66
SW-A1	83	141	32	70	21	70
SW-A2	130	202	43	73	100	177
SW-B1	58	77	10	38	5	9
SW-B2	64	121	27	55	5	10
SW-B3	138	192	80	46	8	21

Fibres with the best solubility (SW-A2 and SW-B3) were then tested, after annealing at varying temperatures, and compared with the comparative examples of Table 1. The results are shown in Table 3.

It can be seen that for the SW-A2 fibre, with increasing annealing temperature, the silica solubility drops progressively. In contrast the SW-B3 composition shows no loss in solubility up to 800°C and although a reduction in solubility is shown above that temperature it is not as dramatic as for SW-A2. Despite this difference in solubility it is to be noted that only the needled GF fibre shows a

comparable silica solubility and that material melts at 700°C.

TABLE 3

Fibre	Condition	Solubility Analyses					
		CaO(ppm)		MgO(ppm)		SiO_2(ppm)	
		5hrs	24hrs	5hrs	24hrs	5hrs	24hrs
SW-A2	As received	58	37	37	3	89	130
SW-A2	600°C, 48hrs	33	56	27	43	60	108
SW-A2	800°C, 48hrs	35	53	17	30	43	87
SW-A2	1000°C, 48hrs	7	3	3	2	11	21
SW-B3	As received	35	69	7	22	22	100
SW-B3	600°C, 48hrs	61	150	12	22	55	130
SW-B3	800°C, 48hrs	41	90	3	7	24	144
SW-B3	1000°C, 48hrs	18	40	3	3	17	60
CRBT	As received	10	8	6	3	5	3
CHBT	As received	16	10	7	3	4	0.3
Glass Fibre	As received	14	17	5	3	5	7
Needled GF	As received	17	34	8	15	66	85
Needled GF	600°C, 48 hrs	11	26	7	10	19	37
Mineral Fibre	As received	16	16	7	6	8	9

[The Glass Fibre and Needled Glass Fibre had the compositions shown in Table 1.]

The user is primarily concerned with the solubility of the fibre as received as it is in this condition that most handling occurs; as received both SW-A2 and SW-B3 fibres have extremely high solubility. Even after exposure to 800°C and 1000°C these fibres have solubilities much higher than other high temperature use fibres.

To investigate the reasons underlying the difference in solubilities after high temperature annealing between the SW-A2 and SW-B3 fibres qualitative X-ray diffraction was done on the fibres. The results are indicated in Table 4 and it can be seen that the SW-B3 fibre forms pseudowollastonite and wollastonite, whereas the SW-A2 fibre forms diopside. It appears therefore that the crystalline diopside has a lower solubility in physiological saline solution than the crystalline pseudowollastonite and wollastonite material precipitated from the SW-B3 fibre.

TABLE 4

Sample	Condition	Qualitative XRD
SW-A2	600°C, 48 hours	Amorphous
SW-A2	800°C, 48 hours	Amorphous with small amount Diopside
SW-A2	1000°C, 48 hours	Diopside
SW-B3	600°C, 48 hours	Amorphous
SW-B3	800°C, 48 hours	Amorphous
SW-B3	1000°C, 48 hours	Pseudowollastonite & Wollastonite

Various of the fibres were then tested for their shrinkage characteristics. Table 5 shows the results of Shrinkage tests on all the test fibres and on some of the comparative fibres. These results were obtained by proposed ISO standard ISO/TC33/SC2/N220 (equivalent to British Standard

BS 1920, part 6,1986) with some modifications to account for small sample size. The method in summary comprises the manufacture of vacuum cast preforms, using 75g of fibre in 500cm^3 of 0.2% starch solution, into a 120 x 65mm tool. Platinum pins (approx 0.1-0.3mm diameter) were placed 100 x 45mm apart in the 4 corners. The longest lengths (L1 & L2) and the diagonals (L3 & L4) were measured to an accuracy of ±0.01mm using a travelling microscope attached to a steel rule with a vernier scale. The samples were placed in a furnace at temperature and left for 24 hours. The shrinkage values are given as an average of the 4 measurements.

TABLE 5

LINEAR SHRINKAGE (%)

(24h at temperature)

Temp. °C	SW-A	SW-A1	SW-A2	SW-B1	SW-B2	SW-B3
730	1.45		1.43	1.02	0.22	
870				0.41		
900			1.07			1.07
1000		1.04	1.3	0.51	0.6	1.1
1100		0.71	1.8		0.73	2.2
Maximum Service Temperature °C	850	1050	1050	1050	1050	1000

It can be seen that in SW-A, SW-A1, SW-A2, SW-B1, SW-B2 and SW-B3, owing to the increase in molar volume on crystallisation, the linear shrinkage at the maximum service temperature is less than 3.5%.

Table 6 shows the results of a further series of shrinkage tests made in the same way.

TABLE 6

Sample	Measurement Direction c.f. Roll Direction	Test Temperatures °C	Linear Shrinkages % Range	Mean
SW-A2	Parallel	850	1.1-1.4	1.2
SW-A2	Perpendicular	850	0.7-1.5	1.3
SW-A2	Parallel	900	0.5-1.1	0.9
SW-A2	Perpendicular	900	1.9-4.5	3.0
SW-A2	Parallel	1000	0.5-2.9	1.3
SW-A2	Perpendicular	1000	1.7-2.9	2.2
SW-A2	Parallel	1100	0.7-1.5	1.0
SW-A2	Perpendicular	1100	1.0-2.6	1.8
SW-B3	Parallel	900	1.6-1.8	1.7
SW-B3	Perpendicular	900	1.4-2.4	2.1
SW-B3	Parallel	1000	1.6-2.3	1.9
SW-B3	Perpendicular	1000	1.0-2.3	1.7
SW-B3	Parallel and Perpendicular	1100	Complete Melting (Lantern type remnant)	

To ascertain the applicability of these tests to long term usage a series of cyclic shrinkage tests were undertaken on the materials and the heating schedule used for these cyclic

tests is shown in Figure 3.

The results of the tests are shown in Tables 7 & 8 (the two figures given for SW-B3 are due to slight differences in chemical analysis [the fibre at the end of a production run of fibre tends to have slightly differing composition to that at the beginning of a production run of fibre]).

As a further comparison with the above discussed materials a melt was made comprising 55% SiO_2, 29.9% CaO and 18.6% MgO. Fibres made using this composition had a maximum service temperature of 700°C and melted at 800°C.

As these results were encouraging the applicants conducted a further and extensive series of tests, concentrating on the SW-A2 and SW-B3 compositions, to ascertain the reproducibility of these results and the boundaries of the useful compositions.

Table 9 (three pages) below gives the compositions of a series of melts, ranked on silica content, and showing the shrinkage figure after exposure to 1000°C for 24 hours (1st column) and 800°C for 24 hours (2nd column). These shrinkages were measured by the same method as the shrinkages given above but measurements were made with a travelling microscope with a digital linear scale accurate to ± 5μm. It can clearly be seen that all fibres with a silica content of less than 58% have a shrinkage at 1000°C of greater than 3.5% save two (B3-3 and 708). These fibres, together with some fibres with a silica content of greater than 58% although showing a reasonable figure at 1000°C, show a very poor figure at 800°C. Compositions with an SiO_2 content of greater than 70% appear to fiberise poorly. This may be because such compositions have two liquids in the melt as may be appreciated from Fig.1

TABLE 7

CYCLIC SHRINKAGE (LINEAR)

(%)

Product	1000°C	1100°C	24h at 1000°C
No. cycles	58	42	
CRBT	2.0	2.7	1.9
CWBT	15.0	13.3	12.1
SW-A2	0.33	2.0	1.3
SW-B3	1.00	1.67	1.1
SW-B3	0.33	0.67	1.1

Accuracy: + or - 0.33%

TABLE 8

CYCLIC SHRINKAGE

(%)

	LINEAR SHRINKAGE			THICKNESS SHRINKAGE	
PRODUCT	1000°C	1100°C	24 h at 1000°C	1000°C	1100°C
No. cycles	104	100		104	100
CRBT	1.47	3.1	1.9	0.47	11.19
CWBT	14.4	15.2	12.1	38.63	32.14
SW-A2	1.5	2.1	1.3	8.58	8.75
SW-B3	1.73	1.63	1.1	7.24	7.57
SW-B3	1.47	1.77	1.1	7.02	7.16

Accuracy: + or - 0.3%(%)

TABLE 9

	Analysed Compositions (Weight %)								Shrinkage at °C		Rationalised Compositions		
Melt	SiO_2%	CaO%	MgO%	Al_2O_3%	Na_2O%	K_2O%	Fe_2O_3%	ZrO_2%	1000	800	SiO_2%	CaO%	MgO%
A2-28	78.07	2.07	17.15	0.15	<0.05	<0.05	0.11	1.76	¶		80.3	2.1	17.6
A2-16	73.43	12.40	10.09	0.19	<0.05	<0.05	0.11	2.23	0.7	*	76.6	12.9	10.5
A2-32	73.09	6.36	19.60	0.23	0.05	<0.05	0.11	0.36	¶		73.8	6.4	19.8
B3-32	72.38	23.43	0.65	0.31	0.31	0.09	0.22	0.72	¶		75.0	24.3	0.7
A2-15	72.25	12.67	12.35	0.11	<0.05	<0.05	0.10	1.24	1.1	*	74.3	13.0	12.7
A2-22	71.48	9.36	16.34	0.33	0.10	<0.05	0.20	0.83	1.1	*	73.6	9.6	16.8
A2-29	71.24	4.46	22.31	0.19	<0.05	<0.05	0.13	1.23	1.8	*1.5	72.7	4.5	22.8
A2-27	71.14	6.77	19.64	0.24	0.08	<0.05	0.13	1.01	1.2	*1.2	72.9	7.0	20.1
B3-28	70.81	18.74	7.03	0.47	0.23	0.07	0.16	0.75	0.2	*	73.3	19.4	7.3
A2-17	70.43	11.58	14.52	0.15	<0.05	<0.05	0.13	1.58	1.3	*	73.0	12.0	15.0
A2-33	70.04	4.61	22.85	0.25	0.11	<0.05	0.12	1.01	¶		71.9	4.7	23.4
B3-18	69.42	23.27	3.76	0.43	0.37	0.06	0.12	0.47	0.4		72.0	24.1	3.9
A2-6	69.29	15.17	12.76	0.07	0.25	<0.05	0.11	1.13	1.5		71.3	15.6	13.1
B3-16	68.74	24.99	1.71	0.65	0.38	0.10	0.24	1.03	0.3	0.2	72.0	26.2	1.8
A2-26	68.65	8.12	19.26	0.29	<0.05	<0.05	0.21	0.98	1.5	1.5	71.5	8.4	20.1
B3-27	68.56	20.98	7.00	0.78	0.35	0.08	0.17	0.79	0.8	0.7	71.0	21.7	7.3
759	68.33	17.45	12.60	<0.05	0.11	<0.05	0.33	<0.05	1.7	1.1	69.5	17.7	12.8
A2-20	68.19	11.58	16.57	0.40	0.19	0.05	0.21	0.91	1.1	1.0	70.8	12.0	17.2
A2-31	67.62	8.45	21.72	0.32	0.09	<0.05	0.15	0.64	2.3	1.9	69.2	8.6	22.2
B3-31	67.59	27.76	0.49	0.40	0.40	0.11	0.22	1.01	0.7		70.5	29.0	0.5
B3-19	67.58	24.91	3.65	0.45	0.37	0.07	0.15	0.65	0.5		70.3	25.9	3.8
B3-17	67.25	26.68	1.86	0.70	0.45	0.10	0.23	0.57	0.3		70.2	27.9	1.9
A2-13	66.67	14.87	16.01	0.11	0.05	<0.05	0.10	0.92	1.6		68.4	15.2	16.4
B3-22	66.17	21.28	9.34	0.52	0.33	0.08	0.18	0.54	1.1	0.8	68.4	22.0	9.6
A2-10	66.17	16.22	15.80	0.49	0.06	<0.05	0.09	<0.05	2.2	1.9	67.4	16.5	16.1
B3-15	65.86	29.82	1.78	0.47	0.45	0.08	0.18	0.51	0.3		67.6	30.6	1.8
719	65.77	25.69	8.12	<0.05	0.24	<0.05	0.23	<0.05	0.5		66.0	25.8	8.2
A2-5	65.69	18.74	13.78	0.18	0.16	<0.05	0.10	0.14	1.9	1.0	66.9	19.1	14.0
B3-4A	65.50	25.81	4.88	2.05	0.28	0.12	0.16	0.24	1.4	1.0			
A2-8	65.33	16.86	14.24	0.22	0.13	<0.05	0.14	1.17	1.5		67.7	17.5	14.8

TABLE 9 (continued)

Melt	Analysed Compositions (Weight %)								Shrinkage at °C		Rationalised Compositions		
	SiO_2%	CaO%	MgO%	Al_2O_3%	Na_2O%	K_2O%	Fe_2O_3%	ZrO_2%	1000	800	SiO_2%	CaO%	MgO%
718	65.23	27.14	6.95	<0.05	0.24	<0.05	0.20	0.49	0.4		65.7	27.3	7.0
B3-14	65.11	24.91	5.54	0.58	0.43	0.09	0.19	0.61	1.0		68.1	26.1	5.8
721	65.08	27.26	5.33	0.06	0.17	<0.05	0.08	<0.05	0.3	0.6	66.6	27.9	5.5
A2-34	64.85	6.63	26.20	0.23	0.06	<0.05	0.16	0.80	3.4	3.9	66.4	6.8	26.8
A2-21	64.16	13.74	19.98	0.34	0.17	<0.05	0.11	0.13	3.2	3.3	65.6	14.0	20.4
B3-30	64.13	31.93	0.37	0.64	0.45	0.09	0.14	0.28	0.6		66.5	33.1	0.4
A2-35	64.12	8.88	24.88	0.29	0.10	<0.05	0.13	0.47	7.3	7.1	65.5	9.1	25.4
B3-23	64.09	23.26	9.33	0.56	0.36	0.09	0.16	0.30	1.0		66.3	24.0	9.7
B3-5A	63.74	25.41	4.68	3.97	0.26	0.12	0.17	0.58	7.4	4.3			
A2-30	63.68	16.06	18.21	0.40	0.11	0.07	0.15	<0.05	2.7	1.6	65.0	16.4	18.6
A2-9	63.66	21.44	12.96	1.49	0.32	0.10	0.11	<0.05	1.9	0.9	64.9	21.9	13.2
A2-12	63.56	16.55	18.00	0.33	0.11	<0.05	0.08	0.05	1.0	2.3	64.8	16.9	18.3
B3-6A	63.24	24.83	4.59	5.70	0.27	0.11	0.15	0.15	21.6	18.8			
723	62.61	29.79	5.44	<0.05	0.17	<0.05	0.13	<0.05	0.4	0.5	64.0	30.4	5.6
757	62.60	20.92	15.22	0.20	<0.05	<0.05	0.16	<0.05	1.3	2.9	63.4	21.2	15.4
A2-25	62.36	10.99	24.18	0.33	0.10	0.05	0.16	0.07	6.1		63.9	11.3	24.8
B3-13	62.33	30.62	2.06	0.55	0.65	0.09	0.17	0.91	0.8	0.9	65.6	32.2	2.2
A2-7	61.98	23.37	11.98	0.44	0.25	<0.05	0.10	0.23	1.4		63.7	24.0	12.3
725	61.83	28.13	7.54	0.10	0.36	<0.05	0.17	<0.05	0.6		63.4	28.9	7.7
B3-11	61.71	33.25	2.33	0.69	0.52	0.12	0.25	0.59	0.9		63.4	34.2	2.4
B3-24	61.62	25.53	9.73	0.58	0.38	0.10	0.17	<0.05	1.8	1.2	63.6	26.4	10.0
A2-24	61.38	13.62	22.74	0.31	0.16	<0.05	0.14	0.08	3.3	12.3	62.8	13.9	23.3
722	61.33	31.08	5.25	0.05	0.20	<0.05	0.16	<0.05	1.3		62.8	31.8	5.4
924	61.32	19.78	14.54	2.57	<0.05	<0.05	0.09	0.66	0.3	3.0	64.1	20.7	15.2
B3-2A	60.83	32.30	0.48	4.15	0.35	0.15	0.19	0.12	7.5	3.3			
A2-14	60.74	25.30	11.66	0.28	0.18	0.05	0.13	0.16	1.8		62.2	25.9	11.9
B3-1A	60.32	32.27	3.99	1.74	0.32	0.10	0.15	0.09	2.5	1.7			
A2-11	60.32	24.28	13.24	0.25	0.18	<0.05	0.09	0.08	1.8	1.1	61.7	24.8	13.5
B3-9	60.28	34.49	2.50	0.76	0.50	0.13	0.28	0.49	1.6	1.7	62.0	35.4	2.6
A2-23	60.20	18.59	18.78	0.48	0.19	0.08	0.15	0.05	18.9	10.7	61.7	19.1	19.2

TABLE 9 (continued)

Melt	Analysed Compositions (Weight %)								Shrinkage at °C		Rationalised Compositions		
	SiO_2%	CaO%	MgO%	Al_2O_3%	Na_2O%	K_2O%	Fe_2O_3%	ZrO_2%	1000	800	SiO_2%	CaO%	MgO%
B3-1	60.11	32.56	3.80	0.79	0.54	0.12	0.23	0.82	0.5		62.3	33.8	3.9
932	59.85	21.60	15.65	1.50	0.06	<0.05	0.18	0.11	12.8		61.6	22.3	16.1
692	59.82	34.34	5.44	0.13	0.19	<0.05	0.08	0.17	2.1		60.0	34.5	5.5
B3-3A	59.54	31.64	0.67	5.91	0.33	0.15	0.21	0.41	43.3	15.3			
B3-25	59.53	28.15	9.22	0.48	0.39	0.08	0.14	<0.05	2.3		61.4	29.1	9.5
B3-29	59.40	36.00	0.68	0.92	0.43	0.14	0.23	0.17	0.9		61.8	37.5	0.7
714	59.05	32.00	8.27	<0.05	0.27	<0.05	0.40	<0.05	0.7	1.2	59.5	32.2	8.3
696	58.81	30.91	6.15	0.21	0.18	<0.05	0.08	0.24	0.3	1.4	61.3	32.3	6.4
A2-19	58.71	18.48	19.74	0.54	0.20	0.07	0.19	<0.05	4.7		60.6	19.0	20.4
586	58.65	35.03	3.90	0.13	0.23	<0.05	0.16	<0.05	1.9	1.6	60.1	35.9	4.0
694	58.39	33.10	6.02	0.27	0.20	<0.05	0.10	0.17	1.6	1.9	59.9	33.9	6.2
765	57.78	3.90	35.07	2.12	<0.05	<0.05	0.23	<0.05	34.2		59.7	4.0	36.3
660	57.74	34.65	4.83	1.15	0.24	<0.05	0.19	<0.05	24.7		59.4	35.6	5.0
B3-20	57.57	32.70	6.07	0.91	0.57	0.13	0.22	<0.05	30.9		59.8	33.9	6.3
712	57.54	35.39	4.61	0.06	0.23	<0.05	0.12	<0.05	4.4	3.4	59.0	36.3	4.7
B3-21	57.38	36.62	2.43	0.73	0.51	0.11	0.16	0.08	30.3		59.5	38.0	2.5
B3-26	56.98	30.50	9.44	0.62	0.44	0.11	<0.05	<0.05	39.8	26.6	58.8	31.5	9.7
A2-18	56.96	26.29	13.01	0.66	0.51	0.10	0.19	<0.05	36.2		59.2	27.3	13.5
971	56.82	23.92	17.36	0.74	0.18	<0.05	0.14	0.05	41.7		57.9	24.4	17.7
734	56.58	23.62	17.05	1.00	0.06	<0.05	0.13	0.05	39.3		58.2	24.3	17.5
973	56.18	24.45	16.81	0.50	0.08	<0.05	0.14	0.05	34.9		57.7	25.1	17.2
B3-3	55.99	36.07	4.44	0.58	0.45	0.09	0.38	1.46	0.3	34.7	58.0	37.4	4.6
708	55.22	42.79	0.77	<0.05	0.31	<0.05	0.12	<0.05	1.1	8.7	55.9	43.3	0.8
71	54.68	24.04	19.66	0.20	0.17	<0.05	0.23	<0.05	51.7		55.6	24.4	20.0

*Poor fibres containing a lot of shot. All other constituents < 0.1%.

¶Too poor to test for solubility or shrinkage

TABLE 10

	Analysed Compositions (Weight %)								Solubilities ppm			Rationalised Compositions		
Melt	SiO_2%	CaO%	MgO%	Al_2O_3%	Na_2O%	K_2O%	Fe_2O_3%	ZrO_2%	SiO_2	CaO	MgO	SiO_2%	CaO%	MgO%
A2-28	78.07	2.07	17.15	0.15	<0.05	<0.05	0.11	1.76	¶			80.3	2.1	17.6
A2-16	73.43	12.40	10.09	0.19	<0.05	<0.05	0.11	2.23	113	45	55	76.6	12.9	10.5
A2-32	73.09	6.36	19.60	0.23	0.05	<0.05	0.11	0.36	¶			73.8	6.4	19.8
B3-32	72.38	23.43	0.65	0.31	0.31	0.09	0.22	0.72	¶			75.0	24.3	0.7
A2-15	72.25	12.67	12.35	0.11	<0.05	<0.05	0.10	1.24	105	35	48	74.3	13.0	12.7
A2-22	71.48	9.36	16.34	0.33	0.10	<0.05	0.20	0.83	126	36	75	73.6	9.6	16.8
A2-29	71.24	4.46	22.31	0.19	<0.05	<0.05	0.13	1.23	94	21	105	72.7	4.5	22.8
A2-27	71.14	6.77	19.64	0.24	0.08	<0.05	0.13	1.01	101	24	67	72.9	7.0	20.1
B3-28	70.81	18.74	7.03	0.47	0.23	0.07	0.16	0.75	108	49	31	73.3	19.4	7.3
A2-17	70.43	11.58	14.52	0.15	<0.05	<0.05	0.13	1.58	91	35	72	73.0	12.0	15.0
A2-33	70.04	4.61	22.85	0.25	0.11	<0.05	0.12	1.01	¶			71.9	4.7	23.4
B3-18	69.42	23.27	3.76	0.43	0.37	0.06	0.12	0.47	145	66	17	72.0	24.1	3.9
A2-6	69.29	15.17	12.76	0.07	0.25	<0.05	0.11	1.13	152	48	70	71.3	15.6	13.1
B3-16	68.74	24.99	1.71	0.65	0.38	0.10	0.24	1.03	132	72	10	72.0	26.2	1.8
A2-26	68.65	8.12	19.26	0.29	<0.05	<0.05	0.21	0.98	183	31	97	71.5	8.4	20.1
B3-27	68.56	20.98	7.00	0.78	0.35	0.08	0.17	0.79	122	54	20	71.0	21.7	7.3
759	68.33	17.45	12.60	<0.05	0.11	<0.05	0.33	<0.05	117	38	40	69.5	17.7	12.8
A2-20	68.19	11.58	16.57	0.40	0.19	0.05	0.21	0.91	162	31	69	70.8	12.0	17.2
A2-31	67.62	8.45	21.72	0.32	0.09	<0.05	0.15	0.64	103	26	72	69.2	8.6	22.2
B3-31	67.59	27.76	0.49	0.40	0.40	0.11	0.22	1.01	112	50	4	70.5	29.0	0.5
B3-19	67.58	24.91	3.65	0.45	0.37	0.07	0.15	0.65	163	44	21	70.3	25.9	3.8
B3-17	67.25	26.68	1.86	0.70	0.45	0.10	0.23	0.57	162	49	13	70.2	27.9	1.9
A2-13	66.67	14.87	16.01	0.11	0.05	<0.05	0.10	0.92	159	47	70	68.4	15.2	16.4
A2-10	66.17	16.22	15.80	0.49	0.06	<0.05	0.09	<0.05	122	42	52	67.4	16.5	16.1
B3-22	66.17	21.28	9.34	0.52	0.33	0.08	0.18	0.54	174	62	57	68.4	22.0	9.6
B3-15	65.86	29.82	1.78	0.47	0.45	0.08	0.18	0.51	156	38	7	67.6	30.6	1.8
719	65.77	25.69	8.12	<0.05	0.24	<0.05	0.23	<0.05	115	51	24	66.0	25.8	8.2
A2-5	65.69	18.74	13.78	0.18	0.16	<0.05	0.10	0.14	150	48	60	66.9	19.1	14.0
B3-4A	65.50	25.81	4.88	2.05	0.28	0.12	0.16	0.24	82	52	16			
A2-8	65.33	16.86	14.24	0.22	0.13	<0.05	0.14	1.17	181	54	84	67.7	17.5	14.8

TABLE 10 (continued)

	Analysed Compositions (Weight %)								Solubilities ppm			Rationalised Compositions		
Melt	SiO_2%	CaO%	MgO%	Al_2O_3%	Na_2O%	K_2O%	Fe_2O_3%	ZrO_2%	SiO_2	CaO	MgO	SiO_2%	CaO%	MgO%
718	65.23	27.14	6.95	<0.05	0.24	<0.05	0.20	0.49	107	47	20	65.7	27.3	7.0
B3-14	65.11	24.91	5.54	0.58	0.43	0.09	0.19	0.61	158	67	27	68.1	26.1	5.8
721	65.08	27.26	5.33	0.06	0.17	<0.05	0.08	<0.05	153	68	20	66.6	27.9	5.5
A2-34	64.85	6.63	26.20	0.23	0.06	<0.05	0.16	0.80	39	11	119	66.4	6.8	26.8
A2-21	64.16	13.74	19.98	0.34	0.17	<0.05	0.11	0.13	160	28	56	65.6	14.0	20.4
B3-30	64.13	31.93	0.37	0.64	0.45	0.09	0.14	0.28	163	83	3	66.5	33.1	0.4
A2-35	64.12	8.88	24.88	0.29	0.10	<0.05	0.13	0.47	61	18	106	65.5	9.1	25.4
B3-23	64.09	23.26	9.33	0.56	0.36	0.09	0.16	0.30	101	44	31	66.3	24.0	9.7
B3-5A	63.74	25.41	4.68	3.97	0.26	0.12	0.17	0.58	48	43	11			
A2-30	63.68	16.06	18.21	0.40	0.11	0.07	0.15	<0.05	102	33	52	65.0	16.4	18.6
A2-9	63.66	21.44	12.96	1.49	0.32	0.10	0.11	<0.05	195	67	66	64.9	21.9	13.2
A2-12	63.56	16.55	18.00	0.33	0.11	<0.05	0.08	0.05	160	47	66	64.8	16.9	18.3
B3-6A	63.24	24.83	4.59	5.70	0.27	0.11	0.15	0.15	26	7	26			
723	62.61	29.79	5.44	<0.05	0.17	<0.05	0.13	<0.05	141	62	17	64.0	30.4	5.6
757	62.60	20.92	15.22	0.20	<0.05	<0.05	0.16	<0.05	187	62	73	63.4	21.2	15.4
A2-25	62.36	10.99	24.18	0.33	0.10	0.05	0.16	0.07	160	35	105	63.9	11.3	24.8
B3-13	62.33	30.62	2.06	0.55	0.65	0.09	0.17	0.91	151	41	7	65.6	32.2	2.2
A2-7	61.98	23.37	11.98	0.44	0.25	<0.05	0.10	0.23	178	59	63	63.7	24.0	12.3
725	61.83	28.13	7.54	0.10	0.36	<0.05	0.17	<0.05	186	76	35	63.4	28.9	7.7
B3-11	61.71	33.25	2.33	0.69	0.52	0.12	0.25	0.59	162	28	15	63.4	34.2	2.4
B3-24	61.62	25.53	9.73	0.58	0.38	0.10	0.17	<0.05	185	37	57	63.6	26.4	10.0
A2-24	61.38	13.62	22.74	0.31	0.16	<0.05	0.14	0.08	136	27	87	62.8	13.9	23.3
722	61.33	31.08	5.25	0.05	0.20	<0.05	0.16	<0.05	185	81	23	62.8	31.8	5.4
924	61.32	19.78	14.54	2.57	<0.05	<0.05	0.09	0.66	77	36	37	64.1	20.7	15.2
B3-2A	60.83	32.30	0.48	4.15	0.35	0.15	0.19	0.12	58	61	5			
A2-14	60.74	25.30	11.66	0.28	0.18	0.05	0.13	0.16	127	57	43	62.2	25.9	11.9
B3-1A	60.32	32.27	3.99	1.74	0.32	0.10	0.15	0.09	119	72	16			
A2-11	60.32	24.28	13.24	0.25	0.18	<0.05	0.09	0.08	149	54	51	61.7	24.8	13.5
B3-9	60.28	34.49	2.50	0.76	0.50	0.13	0.28	0.49	175	8	5	62.0	35.4	2.6
A2-23	60.20	18.59	18.78	0.48	0.19	0.08	0.15	0.05	192	35	47	61.7	19.1	19.2

TABLE 10 (continued)

Melt	Analysed Compositions (Weight %)								Solubilities ppm			Rationalised Compositions		
	SiO_2%	CaO%	MgO%	Al_2O_3%	Na_2O%	K_2O%	Fe_2O_3%	ZrO_2%	SiO_2	CaO	MgO	SiO_2%	CaO%	MgO%
B3-1	60.11	32.56	3.80	0.79	0.54	0.12	0.23	0.82	146	84	17	62.3	33.8	3.9
932	59.85	21.60	15.65	1.50	0.06	<0.05	0.18	0.11	92	41	43	61.6	22.3	16.1
692	59.82	34.34	5.44	0.13	0.19	<0.05	0.08	0.17	140	67	23	60.0	34.5	5.5
B3-3A	59.54	31.64	0.67	5.91	0.33	0.15	0.21	0.41	30	25	10			
B3-25	59.53	28.15	9.22	0.48	0.39	0.08	0.14	<0.05	133	48	33	61.4	29.1	9.5
B3-29	59.40	36.00	0.68	0.92	0.43	0.14	0.23	0.17	201	29	5	61.8	37.5	0.7
714	59.05	32.00	8.27	<0.05	0.27	<0.05	0.40	<0.05	142	73	30	59.5	32.2	8.3
696	58.81	30.91	6.15	0.21	0.18	<0.05	0.08	0.24	163	48	37	61.3	32.3	6.4
A2-19	58.71	18.48	19.74	0.54	0.20	0.07	0.19	<0.05	125	42	66	60.6	19.0	20.4
586	58.65	35.03	3.90	0.13	0.23	<0.05	0.16	<0.05	182	54	19	60.1	35.9	4.0
694	58.39	33.10	6.02	0.27	0.20	<0.05	0.10	0.17	133	66	27	59.9	33.9	6.2
765	57.78	3.90	35.07	2.12	<0.05	<0.05	0.23	<0.05	100	16	169	59.7	4.0	36.3
660	57.74	34.65	4.83	1.15	0.24	<0.05	0.19	<0.05	152	69	23	59.4	35.6	5.0
B3-20	57.57	32.70	6.07	0.91	0.57	0.13	0.22	<0.05	181	29	40	59.8	33.9	6.3
712	57.54	35.39	4.61	0.06	0.23	<0.05	0.12	<0.05	160	24	22	59.0	36.3	4.7
B3-21	57.38	36.62	2.43	0.73	0.51	0.11	0.16	0.08	175	25	16	59.5	38.0	2.5
B3-26	56.98	30.50	9.44	0.62	0.44	0.11	<0.05	<0.05	149	64	41	58.8	31.5	9.7
A2-18	56.96	26.29	13.01	0.66	0.51	0.10	0.19	<0.05	161	47	57	59.2	27.3	13.5
971	56.82	23.92	17.36	0.74	0.18	<0.05	0.14	0.05	142	55	73	57.9	24.4	17.7
734	56.58	23.62	17.05	1.00	0.06	<0.05	0.13	0.05	135	52	66	58.2	24.3	17.5
973	56.18	24.45	16.81	0.50	0.08	<0.05	0.14	0.05	102	42	47	57.7	25.1	17.2
B3-3	55.99	36.07	4.44	0.58	0.45	0.09	0.38	1.46	185	14	18	58.0	37.4	4.6
708	55.22	42.79	0.77	<0.05	0.31	<0.05	0.12	<0.05	193	31	2	55.9	43.3	0.8
71	54.68	24.04	19.66	0.20	0.17	<0.05	0.23	<0.05	133	55	62	55.6	24.4	20.0

There are several anomalies, namely compositions B3-6A, A2-25, A2-24, A2-23, B3-2A, B3-3A, A2-19, and 932. All of these have an SiO_2 content of > 58% but a high shrinkage.

On the assumption that the minimum silica level for satisfactory shrinkage varies with MgO content the applicants have determined that fibres with a silica content (in weight percent) that fail to meet the following expression do not have satisfactory shrinkages at either or both 800°C and 1000°C:-

SiO_2	>58%	- (for MgO =< 10%) and
SiO_2	>58% + 0.5(%MgO -10)	- (for MgO >= 10%)

The applicants have further found that the Al_2O_3 content is important. From their studies it appears that the maximum Al_2O_3 content lies somewhere between 2.57% and 3.97%. The applicants have found that with increasing alumina levels the first material to crystallise is calcium aluminate and this possibly forms a liquid phase that assists flow and hence shrinkage.

Table 10 shows, for the same compositions as Table 9, 24 hour solubilities for each major constituent. It can be seen that all of the compositions have high solubilities.

As mentioned above use of CaO in forming calcium containing fibres is inconvenient and can be hazardous. The applicants investigated use of mixed oxide materials that would avoid the handling of CaO. A fibre was made by admixture of magnesia with silica and wollastonite ($CaSiO_3$).

The raw materials used to make the melt comprised:-

Pennine Darlington Heavy Magnesia (#200)

MgO	-	92.60%
CaO	-	1.75%
Fe_2O_3	-	0.04%
SiO_2	-	0.20%
Cl	-	0.25%
SO_3	-	0.70%
LOI	-	4.50%

Partek's Finnish Low Iron Wollastonite (#200)
(U.K. agent - Cornelius Chemical Co., Romford, Essex)

SiO_2	-	51.80%
CaO	-	44.50%
MgO	-	0.80%
Al_2O_3	-	0.60%
Fe_2O_3	-	0.30%
Na_2O	-	0.10%
K_2O	-	0.05%
TiO_2	-	0.05%
S	-	0.02%
MnO	-	0.01%
P	-	0.01%
F	-	0.01%
LOI	-	1.70%

Hepworth Mineral's Redhill T washed silica sand

SiO_2	-	99.0% min.

These constituents were mixed as 78.65% Wollastonite; 19.25% SiO_2; and 3.6% MgO. This gave 0.4 - 0.5% of the final melt as Al_2O_3.

It was surprisingly found that in producing a melt using these constituents the current requirements were only two-thirds that for the use of the raw oxides.

Fibre was produced by blowing (although spinning and other methods can be used). 2 runs were performed with different blowing conditions.

Chemical analysis was undertaken by the Analytical Department at the applicant's subsidiary Morgan Materials Technology (hereinafter called M^2T) using wet chemical techniques. Fibre diameters were measured using M^2T's Galai particle analyser, with shape analysis software. Typically 40,000 fibres were analysed for each run.

The first result of note was the speed of melt reaction when using wollastonite as compared with lime. Also the current was seen to be very stable throughout the growth of the melt. If the current was lost whilst pulling the electrodes apart the current could be restored simply by pushing them back together again. This was not possible with the runs using lime.

Chemical Analysis

	Others	CaO	MgO	Al_2O_3	SiO_2	ZrO_2	Na_2O	Total
Run1	0.7	32.6	3.8	0.8	60.1	0.8	0.5	99.3
Run2	0.7	32.5	3.8	0.8	60.1	0.8	0.6	99.3

Runs 1 and 2 indicate the respective x-ray fluorescence analyses for each run.

Shrinkage Results (1000°C for 24 hours)

	L1	L2	L3	L4	Av.	Std.Dev.
Run 1	0.9	0.2	0.4	0.6	0.5	0.3
Run 2(A)	1.0	-0.2	0.7	0.6	0.5	0.5
Run 2(B)	0.5	0.2	0.0	0.4	0.2	0.2

Solubility Results (ppm)

	CaO	MgO	SiO_2
Run 1(5 hr)	67	10	95
Run 1(24hr)	84	17	146
Run 2(5hr)	39	7	72
Run 2(24hr)	73	17	186

Fibre diameters

	Mean	Median	100%<	%>5μm	%<1μm
Run 1	5.1μm	3.4μm	30μm	33%	13%
Run 2	4.1μm	2.7μm	25μm	25%	19%

Accordingly it appears to be the case that by using what are cheaper ingredients than the pure oxides one can obtain a fibre that has as high a performance as using purer oxides and at much improved energy costs and safety. It is to be noted that this feature of the invention is not limited to saline soluble fibres and any oxide fibre that contains both calcium and silicon can advantageously be made with a calcium silicate, wollastonite being merely an example of such a silicate.

The previous description is directed towards high temperature usage of particular saline soluble fibres. The following is directed towards the prediction and use of saline soluble fibres. A series of fritted glass melts were made of the compositions shown in Tables 11A and 11B and quenched in water. Solubilities of the various components of the quenched melt were measured by the previously described method of atomic absorption. The solubilities were normalised to a specific surface area of $0.25m^2$/gram of fibre.

The free energy of hydration was calculated by normalising the chemical analysis to 100 weight %; making the assumption that simple silicates ($MSiO_3$/M_2SiO_3) are present

and calculating the free energy of hydration contribution of each species; and summing to get the total free energy of hydration. The data in Tables 11A & 11B is also presented in Fig.4. It can be seen that the fibres lie on a generally straight line bar four groups of materials that will be explained below.

Table 11 shows in each column the following:-

Fibre reference
Composition
Molar ratios
Moles/100 grams of melt
Species assumed (see below)
Calculated free energy of hydration of assumed species (kcal/100 grams)(see below)
Calculated free energy of hydration of assumed species (kJ/kg) (see below)
Solubility data (# indicates not measured [see below])
Specific surface area
Normalised solubility data
log normalised solubility

The base data on which calculation of the free energy of hydration was done is set out in Tables 12 which indicates free energies of hydration taken from the literature in the units kcal/mol and kJ/mol.

Table of Free Energy of Hydration Values for Silicate Melts

TABLE 11

Melt Code	Composition Oxide	Composition Wt.%	Composition Rationalized	Moles	Moles in 100g	Species	Moles in 1kg	Free Energy of Hydration (kcal/100g)	Free Energy of Hydration (kJ/kg)	Solubility Oxide	Solubility (ppm)	S.S.A m2/g	Normalized Solubility	Log(norm solub)
CAS10(B) - A	CaO	47.2	47.8	0.852	0.451	$CaSiO_3$	4.51	-7.3	-304.0	CaO	44	0.30	43	1.63
	Al_2O_3	24.5	24.8	0.243	0.243	Al_2O_3	2.43	0.8	31.6	Al_2O_3	0			
	SiO_2	27.1	27.4	0.451	0.401	CaO	4.01	-5.3	-219.7	SiO_2	7			
	Total	98.8	100.0					-11.8	-492.1	Total	51			
CAS10(B) - B	CaO	46.5	47.2	0.842	0.479	$CaSiO_3$	4.79	-7.7	-322.8	CaO	58	0.39	66	1.82
	Al_2O_3	23.7	24.0	0.235	0.235	Al_2O_3	2.35	0.7	30.6	Al_2O_3	1			
	SiO_2	28.4	28.8	0.479	0.363	CaO	3.63	-4.8	-198.9	SiO_2	44			
	Total	98.6	100.0					-11.8	-491.1	Total	103			
CAS10(B) - C	CaO	47.8	48.4	0.863	0.456	$CaSiO_3$	4.56	-7.3	-307.3	CaO	55	0.36	76	1.88
	Al_2O_3	23.9	24.2	0.237	0.237	Al_2O_3	2.37	0.7	30.8	Al_2O_3	0			
	SiO_2	27.1	27.4	0.456	0.407	CaO	4.07	-5.3	-223.0	SiO_2	55			
	Total	98.8	100.0					-11.9	-499.5	Total	110			
CTS(A)	CaO	42.7	44.3	0.790	0.707	$CaSiO_3$	7.07	-11.4	-476.5	CaO	62	0.40	69	1.84
	TiO_2	12.7	13.2	0.165	0.083	CaO	0.83	-1.1	-45.5	TiO_2	0			
	SiO_2	41.0	42.5	0.707	0.165	TiO_2	1.65	2.6	110.4	SiO_2	49			
	Total	96.4	100.0					-9.9	-411.6	Total	111			
$SrSiO_3$	SrO	63.1	64.4	0.622	0.592	$SrSiO_3$	5.92	-14.4	-604.4	SrO	2	0.37	249	2.40
	SiO_2	34.9	35.6	0.592	0.030	SrO	0.30	0.5	-21.7	SiO_2	367			
	Total	98.0	100.0					-14.9	-626.1	Total	369			
$CaSiO_3$	CaO	46.1	46.9	0.836	0.836	$CaSiO_3$	8.36	-13.5	-563.5	CaO	41	0.45	163	2.21
	SiO_2	52.3	53.1	0.884	0.048	SiO_2	0.48	0.3	11.2	SiO_2	253			
	Total	98.4	100.0					-13.2	-552.3	Total	294			
NAS(A)	Na_2O	18.8	18.9	0.305	0.305	Na_2SiO_3	3.05	-8.8	-367.5	Na_2O	#	0.56	4	0.60
	Al_2O_3	39.7	39.8	0.390	0.390	Al_2O_3	3.90	1.2	50.7	Al_2O_3	4			
	SiO_2	41.1	41.3	0.687	0.382	SiO_2	3.82	2.1	89.4	SiO_2	5			
	Total	99.6	100.0					-5.5	-227.4	Total	9			
CAS4	CaO	21.0	20.9	0.373	0.373	$CaSiO_3$	3.73	-6.0	-251.4	CaO	11	0.62	8	0.90
	Al_2O_3	35.4	35.2	0.345	0.345	Al_2O_3	3.45	1.1	44.9	Al_2O_3	4			
	SiO_2	44.2	43.9	0.731	0.358	SiO_2	7.31	2.0	171.1	SiO_2	5			
	Total	100.6	100.0					-2.9	-35.4	Total	20			
MAS(B)	MgO	10.0	10.3	0.256	0.256	$MgSiO_3$	2.56	-3.6	-149.0	MgO	7	0.52	6	0.78
	Al_2O_3	33.7	34.9	0.342	0.342	Al_2O_3	3.42	1.1	44.5	Al_2O_3	2			
	SiO_2	53.0	54.8	0.912	0.656	SiO_2	6.56	3.7	153.5	SiO_2	4			
	Total	96.7	100.0					1.2	49.0	Total	13			
SAS(A)	SrO	29.8	30.5	0.294	0.294	$SrSiO_3$	2.94	-7.2	-300.2	SrO	9	0.50	8	0.90
	Al_2O_3	31.1	31.8	0.312	0.312	Al_2O_3	3.12	1.0	40.6	Al_2O_3	2			
	SiO_2	36.8	37.7	0.627	0.333	SiO_2	3.33	1.9	77.9	SiO_2	5			
	Total	97.7	100.0					-4.3	-181.7	Total	16			
SCS(A)	SrO	35.0	35.1	0.339	0.339	$SrSiO_3$	3.39	-8.3	-346.1	SrO	75	0.41	280	2.45
	CaO	21.0	21.1	0.376	0.376	$CaSiO_3$	3.76	-6.1	-253.4	CaO	30			
	SiO_2	43.6	43.8	0.729	0.014	SiO_2	0.14	0.1	3.3	SiO_2	355			
	Total	99.6	100.0					-14.3	-596.2	Total	460			

Table of Free Energy of Hydration Values for Silicate Melts

TABLE II Continued

Melt Code	Composition			Moles	Moles	Species	Moles	Free Energy of	Free Energy of	Solubility		S.S.A	Normalized	Log(norm
	Oxide	Wt.%	Rationalized		in 100g		in 1kg	Hydration (kcal/100g)	Hydration (kJ/kg)	Oxide	(ppm)	m^2/g	Solubility	solub)
SMAS(A)	SrO	55.0	56.6	0.546	0.296	$SrSiO_3$	2.96	-7.2	-302.2	SrO	57	0.46	38	1.58
	MgO	1.2	1.2	0.030	0.030	MgO	0.30	-0.2	-8.2	MgO	2			
	Al_2O_3	23.7	24.4	0.239	0.239	Al_2O_3	2.39	0.7	31.1	Al_2O_3	5			
	SiO_2	17.3	17.8	0.296	0.250	SrO	2.50	-4.3	-181.0	SiO_2	5			
	Total	97.2	100.0					-11.0	-460.3	Total	69			
SMAS(B)	SrO	55.0	55.9	0.539	0.401	$SrSiO_3$	4.01	-9.8	-409.4	SrO	110	0.39	95	1.98
	MgO	4.8	4.9	0.122	0.122	MgO	1.22	-0.8	-33.2	MgO	15			
	Al_2O_3	14.8	15.1	0.148	0.148	Al_2O_3	1.48	0.5	19.2	Al_2O_3	1			
	SiO_2	23.7	24.1	0.401	0.138	SrO	1.38	-2.4	-99.9	SiO_2	22			
	Total	98.3	100.0					-12.5	-523.3	Total	148			
SMS(A)	SrO	33.0	32.9	0.318	0.318	$SrSiO_3$	3.18	-7.8	-324.7	SrO	147	0.39	212	2.33
	MgO	12.5	12.5	0.310	0.310	$MgSiO_3$	3.10	-4.3	-180.4	MgO	61			
	Al_2O_3	1.0	1.0	0.010	0.010	Al_2O_3	0.10	0.0	1.3	Al_2O_3	0			
	SiO_2	53.8	53.6	0.892	0.264	SiO_2	2.64	1.5	61.8	SiO_2	125			
	Total	100.3	100.0					-10.6	-442.0	Total	331			
SAS(C)	SrO	56.0	56.2	0.542	0.401	$SrSiO_3$	4.01	-9.8	-409.4	SrO	70	0.38	52	1.72
	Al_2O_3	19.7	19.7	0.193	0.193	Al_2O_3	1.93	0.6	25.1	Al_2O_3	1			
	SiO_2	24.0	24.1	0.401	0.141	SrO	1.41	-2.4	-102.1	SiO_2	8			
	Total	99.7	100.0					-11.6	-486.4	Total	79			
CMAS(A)	CaO	35.0	34.6	0.617	0.293	$CaSiO_3$	2.93	-4.7	-197.5	CaO	11	0.30	24	1.38
	MgO	4.5	4.4	0.109	0.109	MgO	1.09	-0.7	-29.6	MgO	7			
	Al_2O_3	44.0	43.4	0.426	0.426	Al_2O_3	4.26	1.3	55.4	Al_2O_3	3			
	SiO_2	17.8	17.6	0.293	0.324	CaO	3.24	-4.2	-177.6	SiO_2	8			
	Total	101.3	100.0					-8.3	-349.3	Total	29			
SWA2	CaO	21.7	21.7	0.387	0.387	$CaSiO_3$	3.87	-6.2	-260.8	CaO	53	0.48	119	2.08
	MgO	15.7	15.7	0.389	0.389	$MgSiO_3$	3.89	-5.4	-226.4	MgO	57			
	Al_2O_3	0.8	0.8	0.008	0.008	Al_2O_3	0.08	0.0	1.0	Al_2O_3	0			
	SiO_2	61.8	61.8	1.028	0.252	SiO_2	2.52	1.4	59.0	SiO_2	118			
	Total	100.0	100.0					-10.2	-427.2	Total	228			
SAS(D)	SrO	56.5	57.3	0.553	0.413	$SrSiO_3$	4.13	-10.1	-421.7	SrO	107	0.40	92	1.96
	Al_2O_3	17.6	17.9	0.176	0.176	Al_2O_3	1.76	0.5	22.9	Al_2O_3	1			
	SiO_2	24.4	24.8	0.413	0.140	SrO	1.40	-2.4	-101.4	SiO_2	39			
	Total	98.5	100.0					-12.0	-500.2	Total	147			
KMAS(A)	K_2O	16.5	16.5	0.175	0.175	K_2SiO_3	1.75	-7.3	-305.4	K_2O	#	0.36	14	1.15
	MgO	13.0	13.0	0.323	0.323	$MgSiO_3$	3.23	-2.1	-188.0	MgO	8			
	Al_2O_3	18.0	17.9	0.176	0.176	Al_2O_3	1.76	0.5	22.9	Al_2O_3	1			
	SiO_2	52.8	52.6	0.875	0.377	SiO_2	8.75	2.1	204.8	SiO_2	11			
	Total	100.3	100.0					-6.8	-265.7	Total	20			

TABLE 12

Relevant oxides	G_{hyd} (kcal/mole)	G_{hyd} (kJ/mol)
$SiO_2 + H_2O \longrightarrow H_2SiO_3$ (vitreous silica)	5.6	23.4
$Al_2O_3 + 3H_2O \longrightarrow 2Al(OH)_3$	3.1	13.0
$MgO + H_2O \longrightarrow Mg(OH)_2$	-6.5	-27.2
$CaO + H_2O \longrightarrow Ca(OH)_2$	-13.1	-54.8
$SrO + H_2O \longrightarrow Sr(OH)_2$	-17.3	-72.4
$Na_2O + H_2O \longrightarrow 2NaOH$	-33.5	-140.2
$K_2O + H_2O \longrightarrow 2KOH$	-46.1	-192.9
$TiO_2 + H_2O \longrightarrow Ti(OH)_2O$	16.0	66.9
$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$	-55.9	-233.9
$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$	-9.8	-41.0
$ZrO_2 + H_2O \longrightarrow Zr(OH)_2O$	-7.1	-29.7
Relevant Silicates		
$Na_2SiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + 2Na^+(aq)$	-28.8	-120.5
$K_2SiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + 2K^+(aq)$	-41.7	-174.5
$MgSiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + Mg^{2+}(aq)$	-13.9	-58.2
$CaSiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + Ca^{2+}(aq)$	-16.1	-67.4
$SrSiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + Sr^{2+}(aq)$	-24.4	-102.1
$BaSiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + Ba^{2+}(aq)$	-37.3	-156.1
$ZnSiO_3 + 2H^+(aq) \longrightarrow H_2SiO_3 + Zn^{2+}(aq)$	-2.4	-10.0
Disilicates		
$Ca_2SiO_4 + 3H^+(aq) \longrightarrow H_2SiO_3 + 2Ca^{2+} + OH^-$	-30.3	-126.8
$Sr_2SiO_4 + 3H^+(aq) \longrightarrow H_2SiO_3 + 2Sr^{2+} + OH^-$	-50.3	-210.5
$Mg_2SiO_4 + 3H^+(aq) \longrightarrow H_2SiO_3 + 2Mg^{2+} + OH^-$	-17.9	-74.9

Although calculations were undertaken assuming the presence of the simplest silicates choice of other silicates (such as disilicates) does not appear to change the calculations much. For example given below is the calculation for an assumed composition which shows only minor differences for the free energy of hydration calculated.

Composition (moles/100g)	0.767 CaO
	0 417 MgO
	0.669 SiO_2

0.384 Ca_2SiO_4	=	-11.6	or	0.433 $CaSiO_3$	=	-7.0
0.285 $MgSiO_3$	=	- 4.0		0.236 $MgSiO_3$	=	-3.3
0.132 MgO	=	- 0.9		0.334 CaO	=	-4.4
		-16.5		0.181 MgO	=	-1.2
						-15.9
			or	0.384 Ca_2SiO_4	=	-11.6
				0.132 Mg_2SiO_4	=	- 2.4
				0.153 $MgSiO_3$	=	- 2.1
						-16.1

The applicants have found that when the free energy of hydration is more negative than -10kcal/100 grams (-418.4kJ/kg) of composition the composition showed high solubility. The compositions where this relationship broke down were those for which the total solubility was not available (for example those materials containing sodium, where any dissolved sodium would be swamped by the sodium in the saline solution) or where the free energy of hydration of the most likely species present was not available from the literature.

As a test of this technique the two examples of European Patent No. 0399320 were examined. The disclosed examples had the compositions:-

Component	Composition 1 Weight percent	Composition 2 Weight percent
SiO_2	60.7	58.5
Al_2O_3	-	5.8
CaO	16.5	3.0
MgO	3.2	-
B_2O_3	3.3	11.0
Na_2O	15.4	9.8
K_2O	0.7	2.9
Iron oxide	0.2	0.1
BaO	-	5.0
ZnO	-	3.9

Using the above method of calculation Composition 1 had a free energy of hydration of -11.6kcal/100grams (-485.3kJ/kg) whereas Composition 2 had a free energy of hydration of -5.8kcal/100grams (-242.6kJ/kg). This would suggest that Composition 1 would be a saline soluble fibre, and hence physiologically safer than an insoluble fibre; whereas Composition 2 would be predicted to be a relatively insoluble fibre and hence less safe. This is what is disclosed in EP 0399320, the fibres of Composition 2 having a longer lifetime in studies in which the fibres were introduced interperitoneally into rats.

As mentioned above this predictive test can fail under some circumstances. To avoid these difficulties the applicants looked to a different predictive technique, namely the assessment of the amount of non-bridging oxygens present. This is calculated by normalising the chemical analysis to 100 weight%; calculating the molar percentage of each oxide; summing the oxygen-weighted contribution of each oxide to get the total number of oxygens; summing the weighted contribution of each oxide of non-bridging oxygens (see below); and taking the ratio of non-bridging oxygens to the total number of oxygens. The applicants have found that when this figure exceeds 30% the fibres are soluble.

To explain the term non-bridging oxygen one must look to the structure of glasses. Glasses are very stiff liquids and to form usually require the presence of a material that can form a network (usually an oxygen-bridged network). The network may be modified by constituents that contribute non-bridging parts to the network and open the structure of the network and so prevent crystallisation. These materials are usually referred to as network-formers and modifiers respectively.

The terms modifier and network former are well known in the glass industries. Network formers are materials such as SiO_2, P_2O_5, B_2O_3 and GeO_2 which can form an interconnected network to form the glassy phase. Modifiers are substances such as CaO, Na_2O, and K_2O which alter the network and have effects on such properties as viscosity and melting point. There are some intermediate materials (such as Al_2O_3, TiO_2, PbO, ZnO and BeO) which can act as both network formers and modifiers depending on the environment and on the amount present.

In the above mentioned test, for calculating the non-bridging oxygens, one ignores the network formers and calculates the contribution of each other oxide. The contribution of each oxide depends on the geometry and charge of each cation in the glass. As examples typical contributions are as follows:-

Ca^{2+},Mg^{2+},Sr^{2+} and other divalent network modifier cations contribute 2 non-bridging oxygens

K^{+},Na^{+} and other monovalent network modifier cations contribute 1 non-bridging oxygen

Al^{3+},Ti^{3+} and other intermediate cations contribute -1 non-bridging oxygen (i.e these oxides <u>reduce</u> the number of non-bridging oxygens)

(Ti^{4+} is reduced to Ti^{3+} in most glasses when present in relatively small quantities)

TABLE 13

Melt Code	Composition		Moles	Mol.%	Oxygen Total	N.B.O.	%N.B.O	Solubility		S.S.A	Normalized Solubility	Log(norm solub)
	Oxide	Wt.%						Oxide	(ppm)	m2/g		
CAS10(B) - A	CaO	47.2	0.842	54.9	160.8	78.4	48.8	CaO	44	0.30	43	1.63
	Al2O3	24.5	0.240	15.7				Al2O3	0			
	SiO2	27.1	0.451	29.4				SiO2	7			
		Total	1.533	100.0				Total	51			
CAS10(B) - B	CaO	46.5	0.829	54.0	160.9	77.8	48.4	CaO	58	0.39	66	1.82
	Al2O3	23.7	0.232	15.1				Al2O3	1			
	SiO2	28.4	0.473	30.8				SiO2	44			
		Total	1.534	100.0				Total	103			
CAS10(B) - C	CaO	47.8	0.852	55.4	159.6	80.4	50.4	CaO	55	0.36	76	1.88
	Al2O3	23.9	0.234	15.2				Al2O3	0			
	SiO2	27.1	0.451	29.3				SiO2	55			
		Total	1.537	100.0				Total	110			
CTS(A)	CaO	42.7	0.761	47.5	152.5	85.1	55.8	CaO	62	0.40	69	1.84
	TiO2	12.7	0.159	9.9				TiO2	0			
	SiO2	41.0	0.682	42.6				SiO2	49			
		Total	1.602	100.0				Total	111			
SrSiO3	SrO	63.1	0.609	51.2	148.8	102.4	68.8	SrO	2	0.37	249	2.40
	SiO2	34.9	0.581	48.8				SiO2	367			
		Total	1.190	100.0				Total	369			
CaSiO3	CaO	46.1	0.822	48.6	151.4	97.2	64.2	CaO	41	0.45	163	2.21
	SiO2	52.3	0.870	51.4				SiO2	253			
		Total	1.692	100.0				Total	294			
NAS(A)	Na2O	18.8	0.303	22.0	228.3	-12.6	-5.5	Na2O	#	0.56	4	0.60
	Al2O3	39.7	0.389	28.3				Al2O3	4			
	SiO2	41.1	0.684	49.7				SiO2	5			
		Total	1.376	100.0				Total	9			
CAS4	CaO	21.0	0.374	25.7	198.1	3.8	1.9	CaO	11	0.62	8	0.90
	Al2O3	35.4	0.347	23.8				Al2O3	4			
	SiO2	44.2	0.736	50.5				SiO2	5			
		Total	1.457	100.0				Total	20			
MAS(B)	MgO	10.0	0.248	17.0	205.6	-11.2	-5.4	MgO	7	0.52	6	0.78
	Al2O3	33.7	0.331	22.6				Al2O3	2			
	SiO2	53.0	0.882	60.4				SiO2	4			
		Total	1.461	100.0				Total	13			
SAS(A)	SrO	29.8	0.288	23.9	201.4	-2.6	-1.4	SrO	9	0.50	8	0.90
	Al2O3	31.1	0.305	25.3				Al2O3	2			
	SiO2	36.8	0.612	50.8				SiO2	5			
		Total	1.205	100.0				Total	16			
SCS(A)	SrO	35.0	0.338	23.5	150.5	99.0	65.8	SrO	75	0.41	280	2.45
	CaO	21.0	0.374	26.0				CaO	30			
	SiO2	43.6	0.726	50.5				SiO2	355			
		Total	1.438	100.0				Total	460			

TABLE13 (continued)

Melt Code	Composition Oxide	Composition Wt.%	Moles	Mol.%	Oxygen Total	N.B.O.	%N.B.O	Solubility Oxide	Solubility (ppm)	S.S.A m2/g	Normalized Solubility	Log(norm solub)
SMAS(A)	SrO	55.0	0.531	49.1	169.6	60.8	35.8	SrO	57	0.46	38	1.58
	MgO	1.2	0.030	2.8				MgO	5			
	Al2O3	23.7	0.232	21.5				Al2O3	2			
	SiO2	17.3	0.288	26.6				SiO2	5			
		Total	1.081	100.0				Total	69			
SMAS(B)	SrO	55.0	0.531	44.6	157.6	84.8	53.8	SrO	110	0.39	95	1.98
	MgO	4.8	0.119	10.0				MgO	15			
	Al2O3	14.8	0.145	12.2				Al2O3	1			
	SiO2	23.7	0.394	33.2				SiO2	22			
		Total	1.189	100.0				Total	148			
SMS(A)	SrO	33.0	0.318	20.7	159.5	80.6	50.5	SrO	147	0.39	212	2.33
	MgO	12.5	0.310	20.2				MgO	61			
	Al2O3	1.0	0.010	0.6				Al2O3	0			
	SiO2	53.8	0.895	58.4				SiO2	123			
		Total	1.533	100.0				Total	331			
SAS(C)	SrO	56.0	0.540	47.7	169.3	61.4	36.3	SrO	70	0.38	52	1.72
	Al2O3	19.7	0.193	17.0				Al2O3	1			
	SiO2	24.0	0.399	35.3				SiO2	8			
		Total	1.132	100.0				Total	79			
CMAS(A)	CaO	35.0	0.624	42.6	179.3	41.4	23.1	CaO	11	0.30	24	1.38
	MgO	4.5	0.112	7.6				MgO	7			
	Al2O3	44.0	0.432	29.5				Al2O3	3			
	SiO2	17.8	0.296	20.3				SiO2	8			
		Total	1.464	100.0				Total	29			
SWA2	CaO	21.7	0.387	21.4	157.5	85.0	54.0	CaO	53	0.48	119	2.08
	MgO	15.7	0.389	21.5				MgO	57			
	Al2O3	0.8	0.008	0.4				Al2O3	0			
	SiO2	61.8	1.028	56.7				SiO2	118			
		Total	1.812	100.0				Total	228			
SAS(D)	SrO	56.5	0.545	48.5	166.9	66.2	39.7	SrO	107	0.40	92	1.96
	Al2O3	17.6	0.173	15.4				Al2O3	1			
	SiO2	24.4	0.406	36.1				SiO2	39			
		Total	1.124	100.0				Total	147			
KMAS(A)	K2O	16.5	0.175	11.3	179.5	41.4	23.1	K2O	#	0.36	14	1.15
	MgO	13.0	0.323	20.8				MgO	8			
	Al2O3	18.0	0.177	11.4				Al2O3	1			
	SiO2	52.8	0.879	56.6				SiO2	11			
		Total	1.554	100.0				Total	20			

Table 13 shows, for the compositions of Table 11, the calculated figure for non-bonding oxygens and these figures are reproduced in Fig.5. It can be seen that the plot of Fig.5 is more linear than that of Fig.4. Compositions with greater than 30% non-bridging oxygens show high solubility.

To illustrate the method the calculation for one example (the first shown in Table 13) is given below:-

	Mols/ Mol	Total Oxygen	Non-bridging Oxygens
CaO	0.549	0.549	1.098 (2*0.549)
Al_2O_3	0.157	0.471 (0.157*3)	-0.314 (-1*0.157*2Al)
SiO_2	0.294	0.588	0.000
	1.000	1.608	0.784

% non-bridging oxygens (0.784/1.608)*100 = 48.8%

As an example one can look to European Patent Specification No. 0399320 referred to above. Using this method in relation to that specification Composition 1 has a non-bridging oxygen percentage of 48.2% whereas Composition 2 has a non-bridging oxygen percentage of 19.6%, again predicting that Composition 1 is more soluble than Composition 2.

There is a further criterion which a composition must meet for it to form vitreous fibres, namely that it be capable of forming a glass. The applicants have found a simple test. If the ratio of modifiers to network formers is less than a critical value (for SiO_2 based glasses, 1) the composition will generally form a glass. For the purpose of this test reasonable results are obtained if such intermediate materials are treated as networkers. Table 14 shows for a series of compositions in each column:-

Fibre reference (N.B. these are not the same fibres as shown in tables 9 & 10)

Composition

Molar ratios

Ratio of glass modifiers to network formers

Free energy of hydration of raw oxides

Melting Point

X-ray diffraction results

Solubility data (# indicates not measured)

Specific surface area

Normalised solubility data

Arbitrary ranking as to solubility and glass forming ability

Indication as to whether melting point above 1500°C

It should be emphasised that this test is a screening one rather than a wholly predictive one as there are several circumstances that may lead to its failure. Among these circumstances are compound formation and inability to quench fast enough to form glass.

Having adopted these tests as a screening method there follows a further step to ascertain whether the composition will form a vitreous fibre. This last step is best examined experimentally as fibre forming ability is a complex function of many physical characteristics, e.g. viscosity, which are often difficult to measure.

<u>Key to Fig.1</u>

CR Cristobalite
TR Tridymite
PS Pseudowollastonite
WO Wollastonite
RA Rankinite
LI Lime
PE Periclase

FO Forsterite
PR Protoenstatite
DI Diopside
AK Akermanite
ME Merwinite
MO Monticellite

TABLE 14

Reference	Composition (Wt. %)	Molar Ratios	Modifier/Networker	Ghyd (kcal/mol)	M. Pt. (C)	XRD Data	Solubility Data (ppm) Species	1 day	Total	5 days	Total	S.S.A. (m2/g)	Norm Solub (0.25 m2/g) 1 day	5 days	Criteria (0-10 Rating) Solub	Glass	M. Pt > 1500C
CASIO(B) No. 18	47.4 CaO	3.8 CaO	0.97	-4.4	1545 (Eut.)	Amorphous + trace (3 small peaks)	CaO	62	124	48	182	0.25	124	182	10	9	Y
	23.4 Al2O3	1.0 Al2O3					Al2O3	7		10							
	29.2 SiO2	1.9 SiO2					SiO2	55		124							
CTS(A) No. 19	42.7 CaO	4.7 CaO	0.85	-1.3	1525 (Eut.)	Amorphous (No peaks)	CaO	100	187	88	197	0.52	83	188	7	10	N
	13.0 TiO2	1.0 TiO2					TiO2	0		0							
	43.6 SiO2	4.5 SiO2					SiO2	87		109							
MAS(A) No. 20	12.5 MgO	1.2 MgO	0.2	3.8	1450 (1400 C)	Amorphous + trace (2 small peaks)	MgO	63	92	248	264	0.57	40	116	4	9	N
	26.5 Al2O3	1.0 Al2O3					Al2O3	5		1							
	62.4 SiO2	4.0 SiO2					SiO2	24		15							
NAS(A) No. 21	29.5 Na2O	1.2 Na2O	0.69	-6.3	1475 (Eut.)	Crystalline (Glassy trace)	Na2O	#	32	#	998	0.53	15	471	1	2	N
	39.2 Al2O3	1.0 Al2O3					Al2O3	3		983							
	33.7 SiO2	1.5 SiO2					SiO2	29		15							
CP1(A) No. 22	53.3 CaO	2.7 CaO	1.35	-24.7	1565 (Eut.)	Crystalline (No glass)	CaO	47	47	17	17	0.68	17	6	1	0	Y
	50.6 P2O5	1.0 P2O5					P2O5	#		#							
SR1(B) No. 23	68.0 SrO	1.1 SrO	1.1	-5.7	1545 (Eut.)	Amorphous (strong) + some crystal. (strong)	SrO	11	1247	5	729	0.88	346	203	10	5	Y
	35.9 SiO2	1.0 SiO2					SiO2	1236		724							
CaSiO3 No. 24	42.3 CaO	1.0 CaO	0.77	-3	1545 (1460 C)	Amorphous + trace (3 small peaks)	CaO	19	1284	27	508	0.71	452	179	10	9	Y
	57.2 SiO2	1.3 SiO2					SiO2	1265		481							
MS1(D) No. 26	37.3 MgO	1.0 MgO	0.91	0.6	1545 (Eut.)	Crystalline (strong) + some glass (strong)	MgO	62	216	249	362	0.83	65	127	5	6	Y
	62.5 SiO2	1.1 SiO2					SiO2	154		113							
C12A17 No. 28	47.7 CaO	11.2 CaO	0.8	-7.2	1400 (Eut.)	Amorphous + trace (Mod. cryst.)	CaO	14	312	3	145	2.45	3.7	15	3	7	N
	53.9 Al2O3	7.0 Al2O3					Al2O3	298		142							
CMS(A) No. 27	62.5 CaO	1.8 CaO	2	-4.3	1575 (Eut.)	Crystalline (No glass)	CaO	42	303	21	227	0.67	150	118	10	6	Y
	16.6 MgO	1.0 MgO					MgO	41		8							
	19.7 SiO2	1.4 SiO2					SiO2	220		198							
CT1(D) No. 25	15.5 CaO	1.0 CaO	4.5700	9.5	1465 (Eut.)	Crystalline (No glass)	CaO	14	14	18	18	1.15	3	3	0	0	N
	77.5 TiO2	3.5 TiO2					TiO2	0		0							
NCS(A) Cryst. No. 29	20.5 Na2O	1.0 Na2O	1.08	-8.7	1425 (Eut.)	Crystalline + some glass (Strong cryst.)	Na2O	#	806	#	375	0.95	204	95	10	4	N
	35.8 CaO	1.9 CaO					CaO	595		333							
	40.8 SiO2	2.1 SiO2					SiO2	211		42							
NCS(A) Glassy No. 30	19.5 Na2O	1.0 Na2O	1.74	-8.1	1425 (Eut.)	Amorphous + some crystal. (8 small peaks)	Na2O	#	686	#	271	1.36	125	49	10	7	N
	35.3 CaO	2.0 CaO					CaO	543		237							
	42.7 SiO2	2.3 SiO2					SiO2	143		34							
CP1(A)Rpt No. 31	54.4 CaO	2.9 CaO	1.45	-24	1565 (Eut.)	Crystalline (No glass)	CaO	14	14	13	13	1.04	3	3	0	0	Y
	48.2 P2O5	1.0 P2O5					P2O5	#		#							
NAS(A) Rpt. No. 32	21.0 Na2O	1.0 Na2O	0.48	-4	1475 (Eut.)	Amorphous (No peaks)	Na2O	#	37	#	50	0.53	17	24	1	10	N
	40.1 Al2O3	1.2 Al2O3					Al2O3	18		30							
	38.7 SiO2	1.8 SiO2					SiO2	19		20							
KAS(E) No. 33	20.0 K2O	1.0 K2O	0.31	-2.7	1590 (Eut.)	Amorphous (No peaks)	K2O	#	28	#	39	0.97	7	10	1	10	Y
	30.4 Al2O3	1.4 Al2O3					Al2O3	9		18							
	46.1 SiO2	3.6 SiO2					SiO2	19		21							
CAS4 No. 34	21.2 CaO	1.1 CaO	0.28	1.1	1550 (1500 C)	Amorphous (No peaks)	CaO	17	28	13	24	0.72	10	8	1	10	Y
	34.0 Al2O3	1.0 Al2O3					Al2O3	1		1							
	44.6 SiO2	2.2 SiO2					SiO2	10		10							
MAS(B) No. 35	14.9 MgO	2.1 MgO	0.24	3.4	1450 (1400 C)	Amorphous (No peaks)	MgO	7	15	68	102	0.61	6	42	1	10	N
	35.9 Al2O3	2.0 Al2O3					Al2O3	1		24							
	51.6 SiO2	4.9 SiO2					SiO2	7		20							
SAS(A) No. 36	32.6 SrO	1.0 SrO	0.25	0.1	1670 (?)	Amorphous (No peaks)	SrO	24	50	1	12	0.67	19	6	2	10	Y
	32.4 Al2O3	1.0 Al2O3					Al2O3	11		1							
	38.1 SiO2	2.0 SiO2					SiO2	15		10							
SCS(A) No. 37	37.1 SrO	1.1 SrO	0.91	-3.6	1400 (Eut)	Amorphous + trace (2 small peaks)	SrO	57	411	3	599	0.57	177	250	10	10	N
	17.5 CaO	1.0 CaO					CaO	35		2							
	43.4 SiO2	2.3 SiO2					SiO2	329		594							

TABLE 14 (continued)

Reference	Composition (Wt. %)	Molar Ratios	Modifier/ Networker	Ghyd (kcal/mol)	M. Pt. (C)	XRD Data	Solubility Data (ppm) Species	1 day	Total	5 days	Total	S.S.A. (m^2/g)	Norm Solub (0.25 m^2/g) 1 day	5 days	Criteria (0-10 Rating) Solub	Glass	M. Pt. ≤ 1500C
SCS(C) No. 38	19.5 SrO 29.4 CaO 47.1 SiO_2	0.5 SrO 1.4 CaO 2.1 SiO_2	0.9	-3.1	1500 (Eut.)	Amorphous (No peaks)	SrO CaO SiO_2	55 36 320	411	11 10 558	579	0.22	155	219	10	10	T
SCS(B) No. 39	51.4 SrO 8.1 CaO 39.7 SiO_2	1.7 SrO 0.5 CaO 2.3 SiO_2	0.97	-4.6	1500 (Eut.)	Amorphous + trace (1 small peak)	SrO CaO SiO_2	5 5 415	425	45 27 507	579	0.86	161	219	10	10	T
SAS(B) No. 40	65.9 SrO 12.4 Al_2O_3 25.0 SiO_2	5.2 SrO 1.0 Al_2O_3 3.4 SiO_2	0.96	-6.6	1600 (?)	Crystalline (strong) + some glass (strong)	SrO Al_2O_3 SiO_2	102 1 350	453	5 1 250	256	0.99	114	65	10	5	T
SMAS(A) No. 41	58.3 SrO 1.1 MgO 25.8 Al_2O_3 18.4 SiO_2	2.3 SrO 0.1 MgO 0.9 Al_2O_3 1.3 SiO_2	0.76	6.2	1610 (1560 C)	Amorphous + trace (1 small peak)	SrO MgO Al_2O_3 SiO_2	87 7 1 9	104	61 4 1 15	81	0.85	40	31	4	10	T
SMAS(B) No. 42	59.1 SrO 3.8 MgO 16.6 Al_2O_3 24.6 SiO_2	6.0 SrO 1.0 MgO 1.7 Al_2O_3 4.3 SiO_2	0.91	-5.8	1610 (1500 C)	Amorphous + trace (3 small peaks)	SrO MgO Al_2O_3 SiO_2	123 32 1 41	197	20 29 1 36	86	0.7	70	31	6	9	T
SMS(A) No. 43	35.9 SrO 0.8 Al_2O_3 12.9 MgO 51.2 SiO_2	1.1 SrO 1.0 MgO 2.7 SiO_2	0.78	-0.4	1600 (1500 C)	Amorphous (No peaks)	SrO MgO SiO_2	159 100 185	444	42 129 177	348	0.75	140	116	10	10	T
SAS(C) No. 44	60.6 SrO 20.7 Al_2O_3 22.6 SiO_2	2.9 SrO 1.0 Al_2O_3 1.9 SiO_2	0.74	-5.9	1600 (?)	Amorphous (No peaks)	SrO Al_2O_3 SiO_2	142 7 18	167	104 7 22	133	0.67	6[illegible]	50	5	10	T
ACPS(A) No 45	16.6 Al_2O_3 39.0 CaO 35.6 P_2O_5 6.7 SiO_2	1.5 Al_2O_3 6.2 CaO 2.2 P_2O_5 1.0 SiO_2	0.74	-17.7	1600 (Eut)	Crystalline (No glass)	Al_2O_3 CaO P_2O_5 SiO_2	1 39 # 6	46	1 35 # 9	45	0.58	20	19	2	0	T
CMAS(A) No. 46	30.6 CaO 5.9 MgO 41.6 Al_2O_3 19.6 SiO_2	1.7 CaO 1.0 MgO 2.8 Al_2O_3 2.2 SiO_2	0.[illegible]	-3.2	1530 (Eut)	Amorphous (No peaks)	CaO MgO Al_2O_3 SiO_2	24 10 2 4	40	21 7 2 9	39	0.54	19	18	2	10	T
SA No. 47	69.1 SrO 32.2 Al_2O_3	2.1 SrO 1.0 Al_2O_3	1.05	-10.7	1500 (Eut)	Crystalline (strong) + some glass (med)	SrO Al_2O_3	49 1106	1155	125 1132	1257	0.62	466	507	10	4	T
SM2A No. 48	21.3 CaO 16.9 MgO 1.1 Al_2O_3 61.5 SiO_2	1.0 CaO 1.1 MgO 2.7 SiO_2	0.78	-0.2	1360	Amorphous (No peaks)	CaO MgO Al_2O_3 SiO_2	70 91 10 151	322	65 116 1 187	369	0.86	122	140	10	10	[illegible]
MAS(C) No. 49	36.9 MgO 25.5 Al_2O_3 41.7 SiO_2	3.5 MgO 1.0 Al_2O_3 2.3 SiO_2	0.73	0	1600 (Eut)	Amorphous (strong) + some cryst. (weak)	MgO Al_2O_3 SiO_2	50 2 7	58	135 2 7	144	0.52	27	67	2	7	T
SAS(D) No. 50	60.3 SrO 16.5 Al_2O_3 22.4 SiO_2	3.6 SrO 1.0 Al_2O_3 2.3 SiO_2	0.84	-6.1	1600 (?)	Amorphous + trace (2 peaks)	SrO Al_2O_3 SiO_2	141 1 118	260	77 1 171	249	0.54	125	117	10	10	T
KMAS(A) No. 51	17.5 K_2O 13.5 MgO 18.4 Al_2O_3 53.1 SiO_2	1.0 K_2O 1.8 MgO 1.0 Al_2O_3 4.8 SiO_2	0.56	-2.4	1500 (Eut)	Amorphous (No peaks)	K_2O MgO Al_2O_3 SiO_2	# 13 1 9	23	# 14 1 10	25	0.94	6	7	1	10	T
KNAS(A) NO.52	20.0 K_2O 9.0 Na_2O 33.8 Al_2O_3 39.9 SiO_2	1.5 K_2O 1.0 Na_2O 2.3 Al_2O_3 4.6 SiO_2	0.54	-6.3	1590 (Eut)	Amorphous (No peaks)	K_2O Na_2O Al_2O_3 SiO_2	# # 14 17	31	# # 32 17	49	0.63	12	19	1	10	T

CLAIMS

1. A method of predicting whether a given composition will form a saline soluble vitreous material, the method comprising the steps of:-

EITHER

a) assuming the composition to be a mixture of the compounds that would be present at equilibrium (on the basis of knowledge, informed belief or reasonable assumption);

b) calculating the sum of the free energies of hydration of each of the compounds assumed to be present;

c) if the sum of the free energies of hydration is more negative than -10 kcal/100grams (-418.4kJ/kg) of composition, assuming the composition to be soluble in saline solution;

OR

a") calculating the percentage of non-bridging oxygens present in relation to the total oxygen present and, if the percentage is greater than 30% assuming the composition to be soluble in saline solution;

2. A method as claimed in claim 1 which further comprises in combination with steps a)-c) and/or a"):-

d) calculating the ratio of glass modifier to network former present;

e) if the ratio is less than a critical value (for SiO_2 based compositions, 1) assuming that the composition will form a vitreous material.

3. A saline soluble vitreous inorganic fibre selected and used in the knowledge that it has a composition meeting the criteria that:-

a) the calculated sum of the free energies of hydration of the compounds that would or could be present at equilibrium (on the basis of knowledge, informed belief or reasonable assumption) is more negative than -10 kcal/100 grams (-418.4kJ/kg) of composition;

and/or

b) the percentage of non-bridging oxygens present in relation to the total oxygen present is greater than 30%.

4. A saline soluble vitreous inorganic fibre as claimed in claim 3 selected and used in the knowledge that it has a composition meeting the criterion that the ratio of glass modifiers to network formers is less than a critical value (for SiO_2 based compositions, 1).

5. Use of a saline soluble vitreous inorganic fibre in the knowledge that it has a composition meeting the criteria that:-

a) the calculated sum of the free energies of hydration of the compounds that would or could be present at equilibrium on the basis of knowledge, informed belief or reasonable assumption is more negative than -10 kcal/100grams (-418.4kJ/kg) of composition;

and/or

b) the calculated percentage of non-bridging oxygens in relation to the total oxygen content is more than 30%.

6. Use as claimed in claim 5 of a saline soluble vitreous inorganic fibre in the knowledge that it has a composition meeting the criterion that the ratio of glass modifiers to network formers is less than a critical value (for SiO_2 based compositions, 1).

7. Use as saline soluble fibres having a shrinkage of less than 3.5% when exposed to 1000°C for 24 hours and/or 800°C for 24 hours, of vitreous fibres having a composition comprising (in weight %):-

SiO_2	>58%	- (for MgO =< 10%) and
SiO_2	>58% + 0.5(%MgO -10)	- (for MgO >= 10%)
CaO	0% - 42%	
MgO	0% - 31.33%	
Al_2O_3	0% - <3.97%	

and being essentially free of fluxing components such as alkali metals and boron oxide.

8. Use as claimed in claim 7 of saline soluble fibres having a shrinkage of less than 3.5% when exposed to 1000°C and/or 800°C for 24 hours, of vitreous fibres in which the amount of SiO_2 is <70%.

9. Use as claimed in any of claims 7-8 of saline soluble fibres having a shrinkage of less than 3.5% when exposed to 1000°C and/or 800°C for 24 hours, the fibres crystallising as diopside and having the composition consisting essentially of:-

<u>Component</u>	Composition A <u>Weight percent</u>
SiO_2	59-64
Al_2O_3	0-3.5
CaO	19-23
MgO	14-17

10. Use as claimed in any of claims 7-8 of saline soluble fibres having a shrinkage of less than 3.5% when exposed to 1000°C and/or 800°C for 24 hours, the fibres crystallising as wollastonite and/or pseudowollastonite and having the composition consisting essentially of:-

Component	Composition B Weight percent
SiO_2	60-67
Al_2O_3	0-3.5
CaO	26-35
MgO	4-6

11. Use as a saline soluble fibre as claimed in any of claims 5-10 and in which, owing to the increase in molar volume on crystallisation, the linear shrinkage at the maximum service temperature is less than 3.5%.

12. A method for the manufacture of refractory oxide fibres containing calcium and silicon by the formation of an oxide melt containing calcium and silicon characterised in that all or part of the calcium and all or part of silicon is provided by a calcium silicate.

13. A method as claimed in claim 13 in which the calcium silicate is wollastonite.

ABSTRACT

Disclosed is use of a vitreous inorganic fibre in the knowledge that it has a composition meeting the criterion that the calculated sum of the free energies of hydration of the compounds that would or could be present at equilibrium (on the basis of knowledge, informed belief or reasonable assumption) is more negative than -10 kcal/100grams of composition. Such compositions are saline soluble.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Gary Anthony Jubb and Jean-Louis Martin

Serial No.: Divisional of 09/262,378

Filing Date: October 24, 2000

For: SALINE SOLUBLE INORGANIC FIBRES

Box Patent Application
Director of Patents and Trademarks
Washington, D.C. 20231

Date: October 24, 2000

TRANSMITTAL OF FORMAL DRAWINGS

Sir:

Applicants transmit herewith three sheets of Formal Drawings in connection with the filing of this divisional application. Applicants paid the issue fee in parent U.S. Serial No. 09/262,378 on September 29, 2000, and at that time provided the U.S. Patent Office with identical Formal Drawings.

Respectfully submitted,

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Reg. No. 35,799

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Attorney Docket No.: M8540/248465

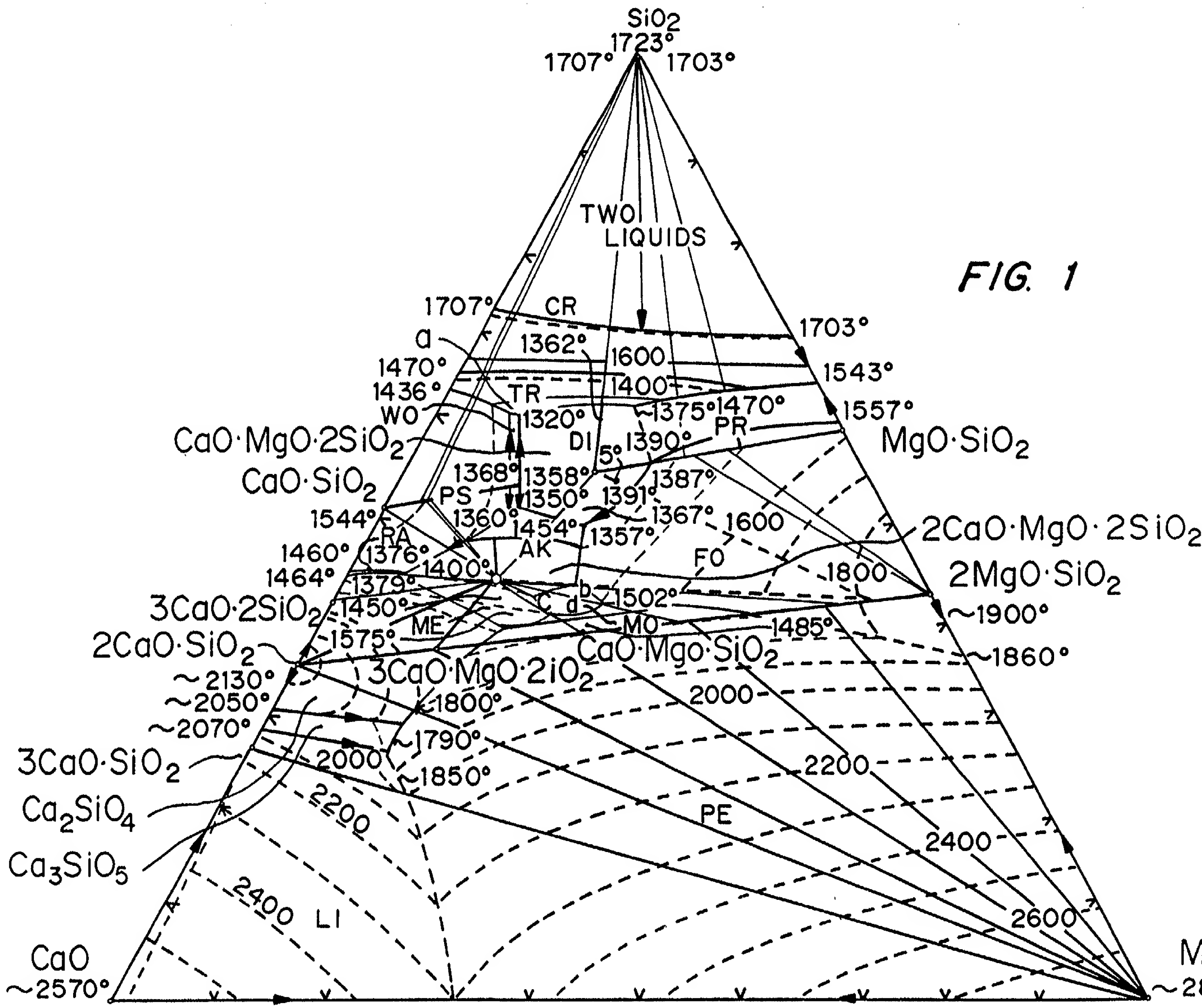

SiO2
1723°
1707°
1703°
TWO LIQUIDS
CR
1707°
1703°
a
1362°
1600
1543°
1470°
1436°
1400
TR
~1375°
1470°
1557°
WO
1320°
PR
CaO·MgO·2SiO2
DI
5°
1390°
MgO·SiO2
CaO·SiO2
1368°
1358°
1387°
PS
1350°
1391°
1544°
1360°
1454°
1367°
1600
2CaO·MgO·2SiO2
RA
1357°
1460°
1376°
AK
FO
1464°
1400°
1800
2MgO·SiO2
1379°
b
1502°
3CaO·2SiO2
1450°
C
d
~1900°
ME
MO
1485°
1575°
2CaO·SiO2
CaO·Mgo·SiO2
~1860°
3CaO·MgO·2iO2
~2130°
~2050°
1800°
2000
~2070°
~1790°
2000
3CaO·SiO2
~1850°
2200
2200
Ca2SiO4
PE
2400
Ca3SiO5
2400
LI
2600
CaO
~2570°
MgO
~2800°

FIG. 1

FIG. 2

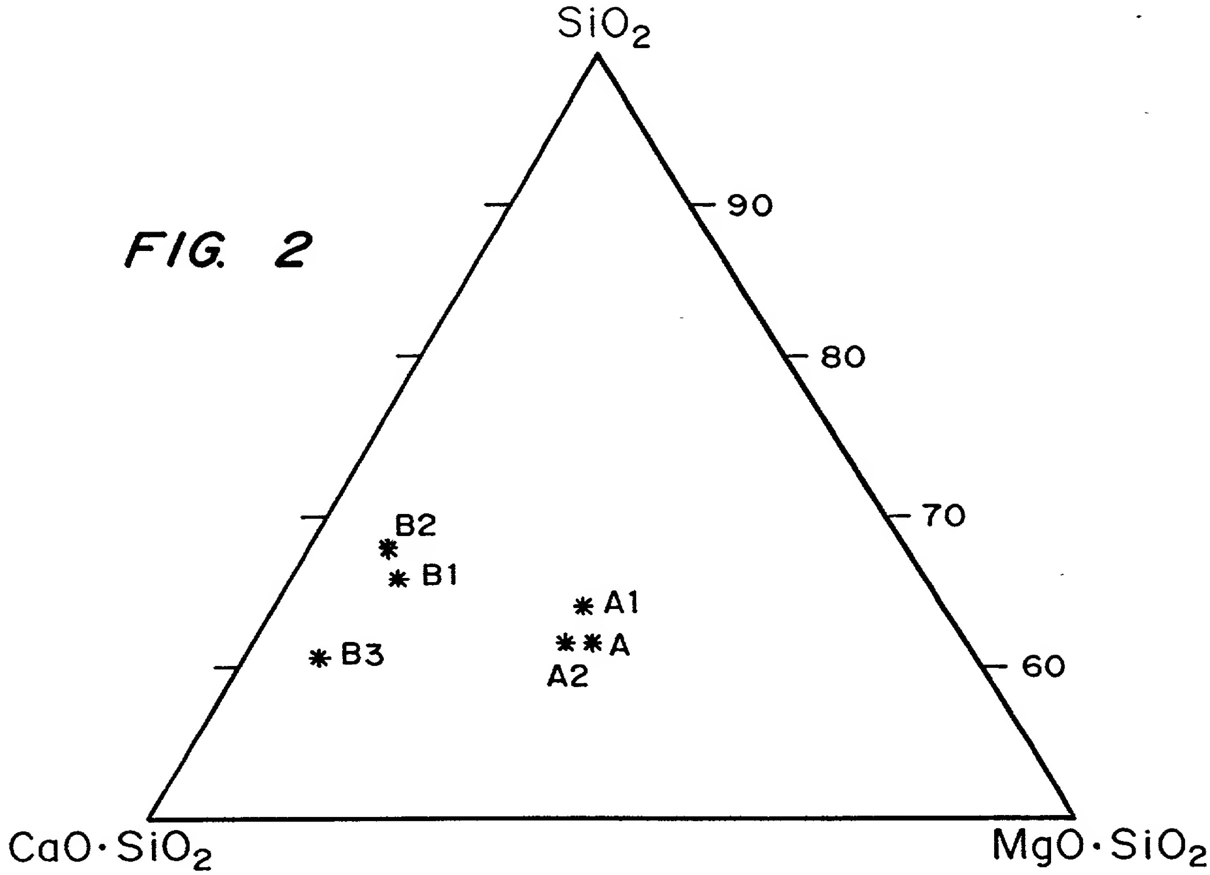
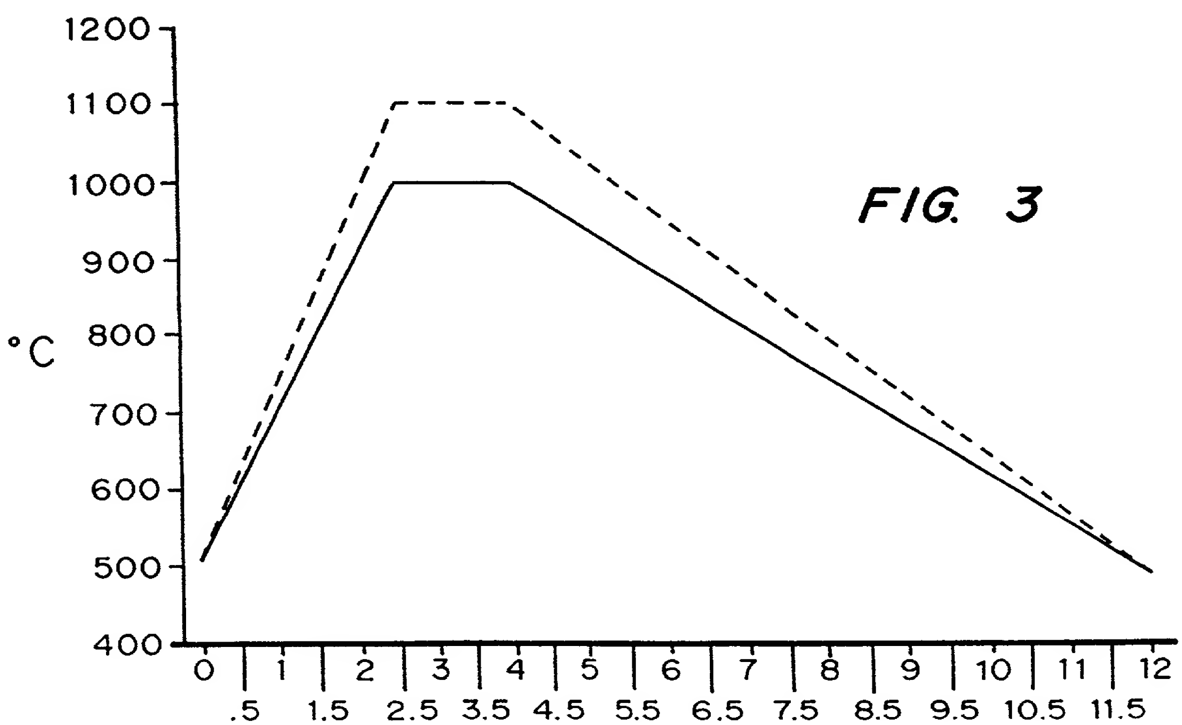

SiO2
CaO·SiO2
MgO·SiO2
90
80
70
60
B2
B1
B3
A1
A
A2

FIG. 3


°C
1200
1100
1000
900
800
700
600
500
400
0 1 2 3 4 5 6 7 8 9 10 11 12
.5 1.5 2.5 3.5 4.5 5.5 6.5 7.5 8.5 9.5 10.5 11.5

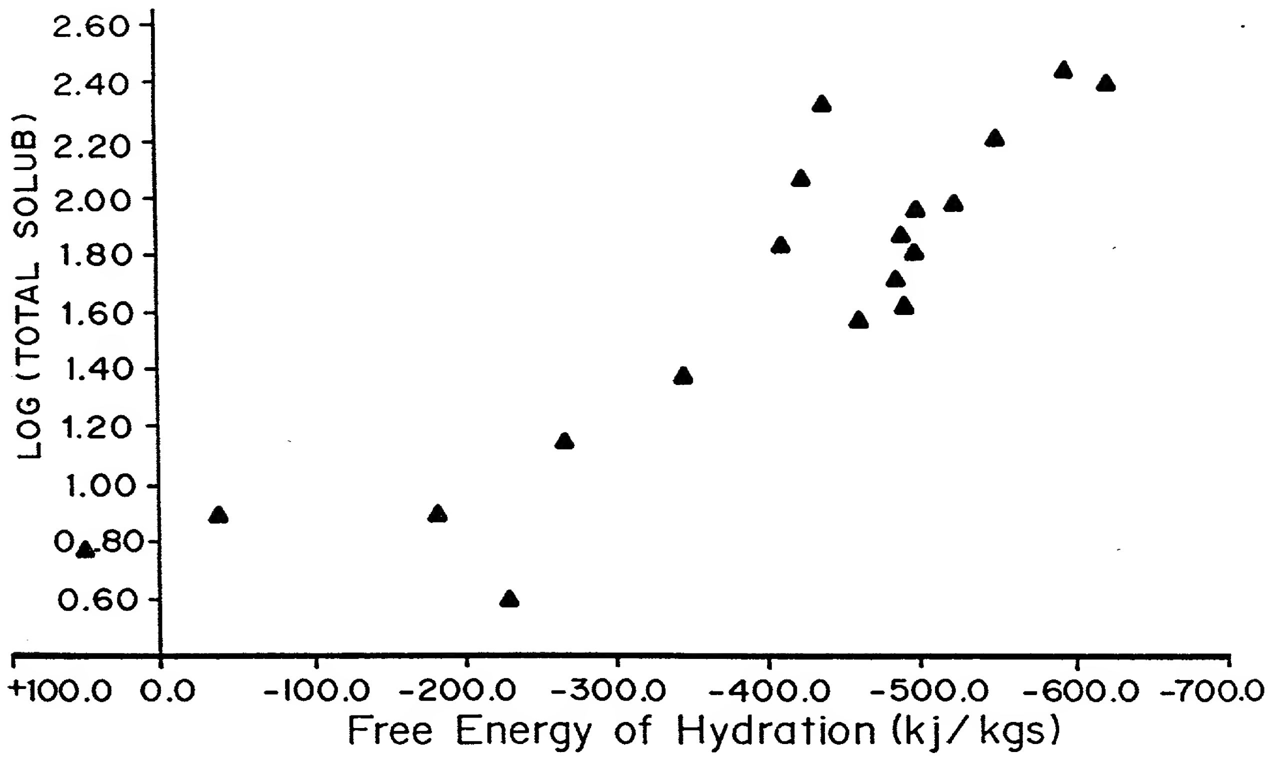

2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
LOG (TOTAL SOLUB)
+100.0
0.0
-100.0
-200.0
-300.0
-400.0
-500.0
-600.0
-700.0
Free Energy of Hydration (kj/kgs)

FIG. 4

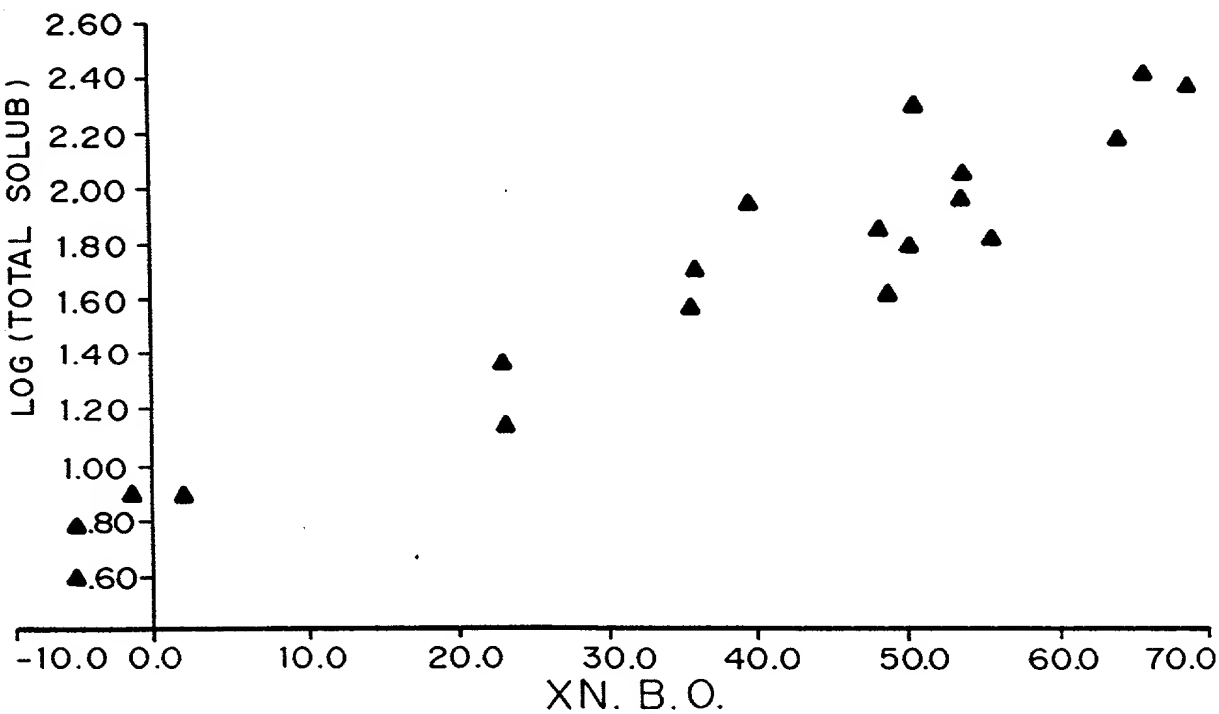

2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
.80
.60
LOG (TOTAL SOLUB)
-10.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
XN. B.O.

FIG. 5

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)	ATTORNEY'S DOCKET NUMBER M8540/188317

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Saline Soluble Inorganic Fibers

the specification of which (check only one item below):

☐ is attached hereto

☒ was filed as United States application
Serial No. 09/262,378
on March 4, 1999
and was amended
on December 21, 1999 (if applicable).

☐ was filed as PCT international application Number
on
and was amended under PCT Article 19
on ______________________ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United State code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
GB	9200993.5	17 January 1992 (17.01.92)	☒ YES ☐ NO
GB	9224612.3	24 November 1992 (24.11.92)	☒ YES ☐ NO
			☐ YES ☐ NO

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(Combined Declaration For Patent Application and Power of Attorney --PTO 1391 [13-11]--page 1 of 2)

903093
COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONTINUED) (Includes Reference to PCT International Applications)	ATTORNEY DOCKET NUMBER M8540/188317

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED
08/535,587	28 September 1995 (28.09.95)			x
08/899,005	23 July 1997 (23.07.97)		x	

PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)	PATENTED	PENDING	ABANDONED
PCT/GB93/00085	15 January 1993 (15.01.93)	08/039,086			x

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(List name and registration number)* Charles Y. Lackey 22,707; John M. Harrington 25,592; John S. Pratt 29,476; A. Jose Cortina 29,733; James L. Ewing, IV 30,630; Charles W. Calkins 31,814; George T. Marcou 33,014; Dean W. Russell 33,452; Richard T. Peterson 35,320; Charles T. Simmons 35,359; Nora M. Tocups 35,717; Bruce D. Gray 35,799; Theodore R. Harper 35,890; Kristin L. Johnson 44,807; Geoff L. Sutcliffe 36,348; Pat Winston Kennedy 36,970; Mitchell G. Stockwell 39,389; Michael J. Turton 40,852; Yonchu L. Kundupoglu 41,130; Benjamin D. Driscoll 41,571; Wilburn L. Chesser 41,668; Alana G. Kriegsman 41,747; J. Steven Gardner 41,772; James J. Bindseil 42,326; Richard H. Lilley 42,803; Edwina Thomas Washington 43,187; Camilla Camp Williams 43,992; Carl B. Massey P44,224; R. Whitney Winston P44,432; John William Ball, Jr. P44,433

Send Correspondence to: John S. Pratt, Esq. Kilpatrick Stockton LLP 1100 Peachtree Street, Suite 2800 Atlanta, GA 30309-4530	Direct Telephone Calls to: (name and telephone number) Bruce D. Gray (404) 815-6218

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2	FULL NAME OF INVENTOR	FAMILY NAME MARTIN	FIRST GIVEN NAME JEAN-LOUIS	SECOND GIVEN NAME
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2	POST OFFICE ADDRESS	POST OFFICE ADDRESS 6 Impasse des Genets	CITY Montbrison	STATE & ZIP CODE/COUNTRY France 42600
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
3	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statement may jeopardize the validity of the application or any patent issuing thereon.

Gary A Jubb Gary Anthony Jubb Date 25/5/2000	Jean-Louis Martin Date 25.05.2000	

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903093
COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

TOTAL P.03

06/01/00 THU 11:34 [TX/RX NO 6512]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS:	Gary Anthony Jubb and Jean-Louis Martin		
SERIAL NO.:	Continuation of 08/899,005	GROUP ART UNIT:	1755
DEPOSIT DATE:	March 4, 1999	EXAMINER:	Karl Group

FOR: SALINE SOLUBLE INORGANIC FIBERS

Assistant Commissioner for Patents
BOX PATENT APPLICATION
Washington, D.C. 20231

Attorney Docket No. 73405DIV

DATE: March 4, 1999

APPOINTMENT OF ASSOCIATE ATTORNEY

Sir:

Please recognize Bruce D. Gray, Reg. No. 35,799 of the firm of Kilpatrick Stockton LLP, 1100 Peachtree Street, Suite 2800, Atlanta, GA 30309-4530 as an Associate Attorney in the above-entitled application.

Respectfully submitted,

Dean W. Russell
Reg. No. 33,452

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ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

NOTE: *If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CIP APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. § 120*

POWER OF ATTORNEY

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (*List name and registration number*)

John S. Pratt, Reg. No. 29,476
James L. Ewing, IV, Reg. No. 30,630
Patrea L. Pabst, Reg. No. 31,284
Jamie Greene, Reg. No. 32,467
Cheryl K. Zalesky, Reg. No. 33,052
Dean W. Russell, Reg. No. 33,452
Charles T. Simmons, Reg. No. 35,359
Daniel M. Epstein, Reg. No. 35,500
Claudia R. Adkison, Reg. No. P36,979

(check the following item, if applicable)

☐ Attached as part of this declaration and power of attorney is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

SEND CORRESPONDENCE TO

John S. Pratt
Kilpatrick & Cody
1100 Peachtree Street
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Atlanta, Georgia 30309
U.S.A.

DIRECT TELEPHONE CALLS TO:
(*Name and telephone number*)

Dean W. Russell
(404) 815-6528

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

Full name of sole or first inventor Gary Anthony Jubb

Gary	Anthony	Jubb
(GIVEN NAME)	(MIDDLE INITIAL OR NAME)	FAMILY (OR LAST NAME)

Inventor's signature Gary A. Jubb

Date 22/3/93 Country of Citizenship U.K.

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(Declaration and Power of Attorney [1-1]—page 4 of 5)

Full name of second joint inventor, if any Jean-Louis Martin

(GIVEN NAME)	(MIDDLE INITIAL OR NAME)	FAMILY (OR LAST NAME)
Jean-Louis	NMI	Martin

Inventor's signature [signature]

Date 25/3/93 Country of Citizenship France

~~Inventor's signature~~ XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

~~Date~~ XXXXXXXXXXXXXXXXXXXXXXXX ~~Country of Citizenship~~ XXXXXXXXXXXXXXXXXXXXXXXX

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United States Patent & Trademark Office

Office of Initial Patent Examination -- Scanning Division

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